

PHOTOCHEMISTRY OF NITRAMINES IV OBSERVED
INTERMEDIATES AND PRODUCTS IN THE
PHOTOCHEMICAL DECOMPOSITION OF
1-NITROPYRROLIDINE

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THESIS

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by

Jhan Craig Swanson

Thesis Advisor:

Charles F. Rowell

June 1973

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Photochemistry of Nitramines IV
Observed Intermediates and Products in the Photochemical
Decomposition of 1-Nitropyrrolidine

by

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ABSTRACT

1-Nitropyrrolidine upon irradiation with ultraviolet light is known to under-go photochemical decomposition. This investigation is concerned with the mechanism and products of the reaction.

A potential intermediate was synthesized and found not detectable in the photochemical system. A product of the photolysis in alkane solutions was identified as an alkyl nitrate. Gas chromatographic analysis and a molecular orbital calculation provided information to suggest processes which might be occurring.

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I. INTRODUCTION

Heterocyclic nitramines have, for a long time, been important as military explosives. In 1967 the photochemical decomposition of HMX, one such explosive, was first observed. To date the mechanism of this photochemical decomposition remains obscure.

Due to the complexity of HMX, it was decided to examine the simpler analog, 1-nitropyrrolidine. A mechanism for the photochemical decomposition of this simpler compound has been proposed by previous workers based upon the presence of nitroxide radicals seen upon irradiation.

This investigation is concerned with the mechanism as proposed by previous workers. Evidence was obtained by photolysis of 1-nitropyrrolidine in alkane solvents followed by gas chromatographic analysis, synthesis of a key intermediate and calculation of energy level spacing by the π approximation.

II. HISTORICAL

Heterocyclic nitramines have, for a long time, been recognized as an important class of high explosives. RDX (Cyclonite, Hexogen, 1,3,5-Trinitro-1,3,5-triazacyclohexane), discovered by Henning in 1899, attained military importance during the second World War, at which time the United States was manufacturing about 15,000 tons per month [1,2]. An explosive with a similar structure, HMX (Octogen, 1,3,5,7-tetranitro-1,3,5,7-tetrazocyclooctane) was isolated and identified in 1941 by Bachmann and Sheehan [3] as an impurity in the nitration of hexamethylene-tetramine to form RDX. As an explosive, HMX was soon found to be superior to RDX because of its higher ignition temperature and greater chemical stability.

Widespread acceptance of these and similar compounds as explosives has generated an interest in their chemical and physical properties which give insight into such practical considerations as thermal stability, shock resistance, "shelf life", and, more recently, such considerations as reclamation of old or damaged explosives and their intentional deactivation. Of particular interest would be mechanistic information on their thermal and photochemical decomposition. While there has been a moderate amount of work in the area, much still remains unknown.

Several studies have been made on the product composition resulting from thermal degradation of HMX. The results of

Robertson [4], Maksinov [5], and Surayanarayana [6] are given below:

TABLE I

PRODUCT COMPOSITIONS FROM
THERMAL DECOMPOSITION OF HMX
(% of total)

	<u>Robertson [3]</u>	<u>Maksinov [4]</u>	<u>Surayanarayana [5]</u>
N ₂ O	38.5		40.0
NO	16.6	Major ^a	9.9
N ₂	18.5		9.6
HCN			4.5
CH ₂ O	Present ^a	Major ^a	8.5
CO ₂	9.4		8.5
CO	16.4		4.1
H ₂ O	Present ^a		

^a Quantity not reported

As a result of an ¹⁵N-tracer study of the decomposition products, Surayanarayana [6] proposed a mechanism (Figure 1) proceeding initially through breakage of the C-N bond rather than the weaker N-N bond.

In 1967, Surayanarayana [7] first observed a photochemical reaction occurring upon irradiation of HMX from an ultraviolet source, although no products were reported. Maycock [8] in 1969 reported the major products to be CH₂O and N₂O, from which he proposed the mechanism given in Figure 2.

Torbit [9] photolysed HMX under varying conditions and found the products to differ significantly from those reported

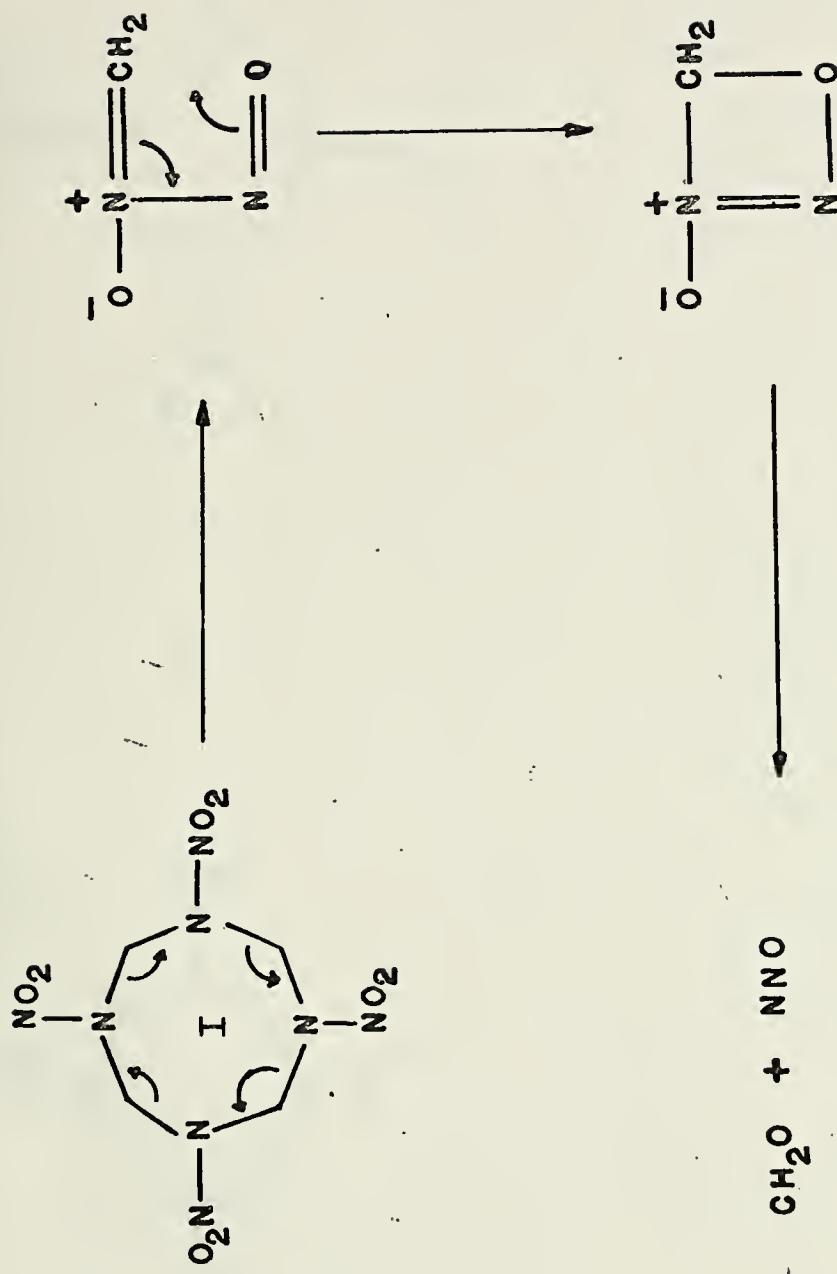


Figure 1. Surayyanarayana's Proposed Mechanism for the Thermal Decomposition of HMX

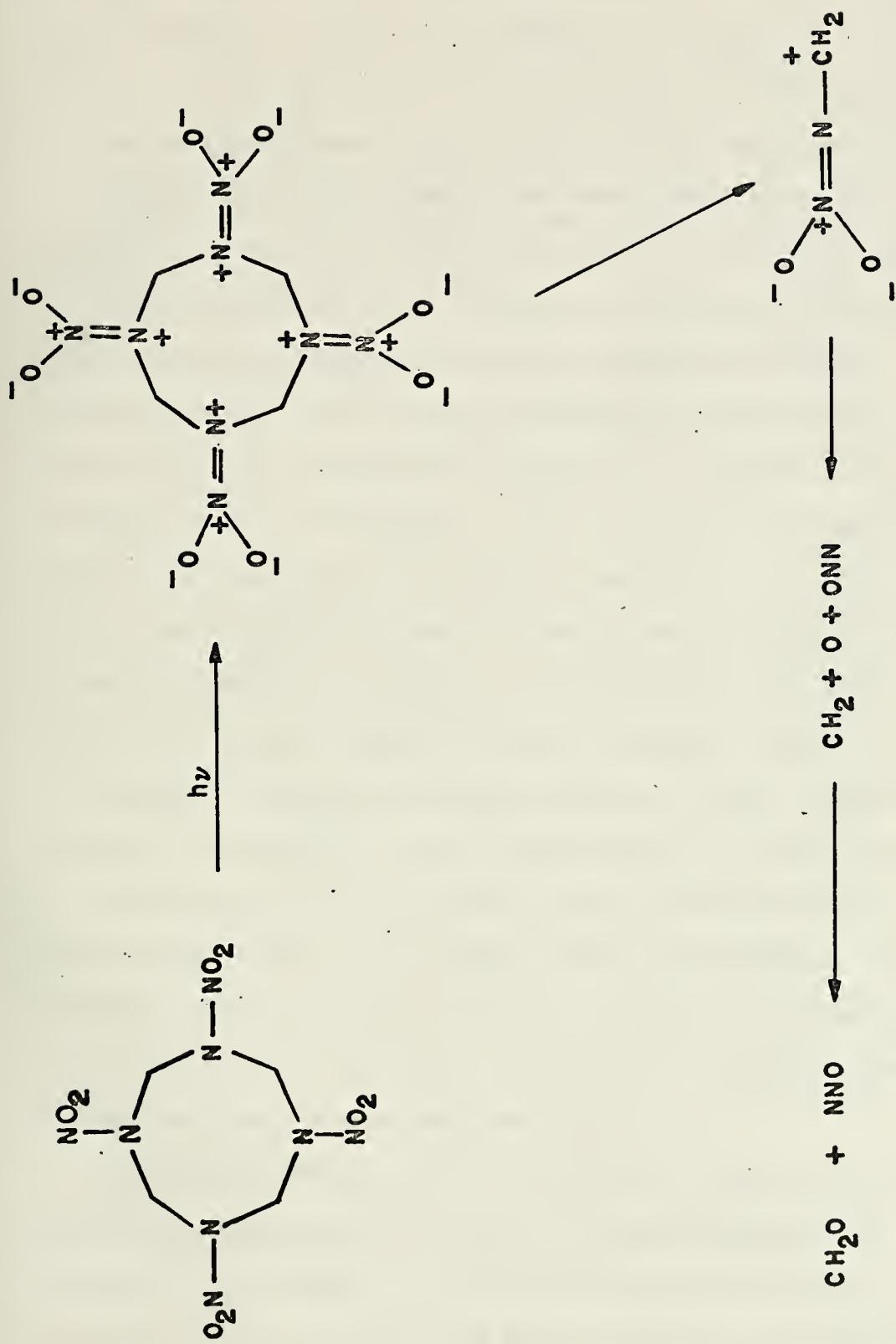


Figure 2. Maycock's Proposed Mechanism for the Photochemical Decomposition of HMX

by Maycock. Solid HMX irradiated in a vacuum gave N_2 , C_2H_4 , and O_2 , while under a helium atmosphere gave N_2 , C_2H_4 , O_2 , CH_2O , and NO_2 . In acetone solution, N_2 , C_2H_2 , O_2 , CO_2 , and N_2O were found, as well as an unidentified solid product.

The mechanism proposed by Torbit is given in Figure 3.

While the above schemes were consistent with the products observed, no direct mechanistic evidence was available.

The presence of four nitramine groups per molecule of HMX makes stepwise mechanistic work extremely difficult. Aside from added complexity, these nitramine groups allow cleavage of the ring in four separate positions, resulting in a variety of small gaseous fragments. Since the four nitramine chromophores are separated by methylene carbons, it seems reasonable that primary photochemical processes would occur independently at one of the four separate, but equivalent sites on the molecule. With these thoughts in mind previous workers [10, 11, 12] decided to examine the photolysis of cyclic unsubstituted aliphatic nitramines, 1-nitropyrrolidine in particular.

Bodnar [10, 13] found that upon irradiation of 1-nitropyrrolidine (II), an ESR signal could be detected, which was assigned to pyrrolidine-1-oxide. Assuming this to be the major photochemical process occurring, a mechanism based upon literature analogs was proposed (Figure 4).

Disproportionation of the nitroxide radical (III) by β -hydrogen abstraction to give the hydroxylamine (IV) and nitrone (V) is common for dialkylnitroxide radicals in general [14, 15, 16, 17] and has been reported by Ingold for this nitroxide in particular [18]. Photochemical oxidation of

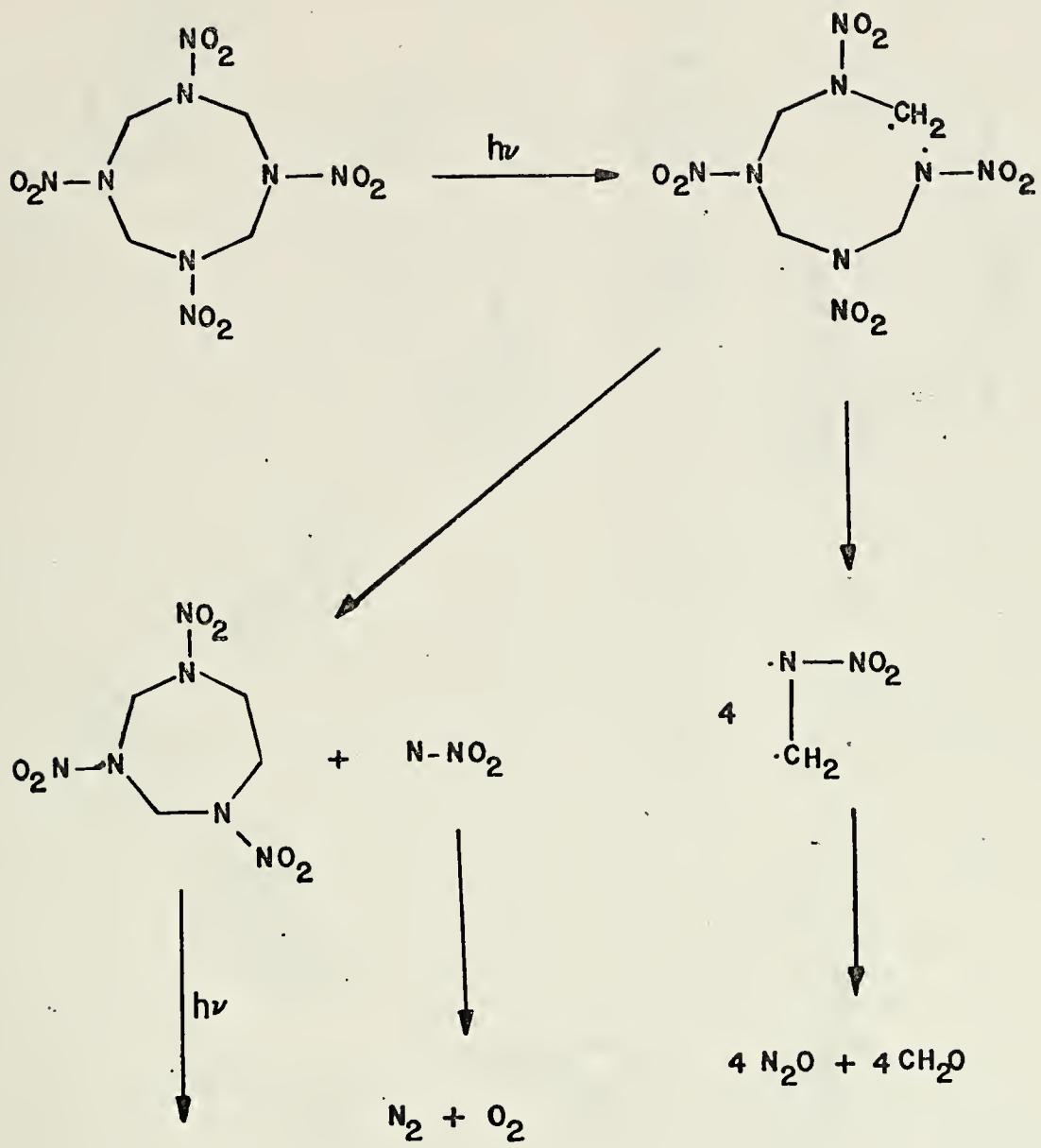


Figure 3. Torbit's Proposed Mechanism for the Thermal Decomposition of HMX

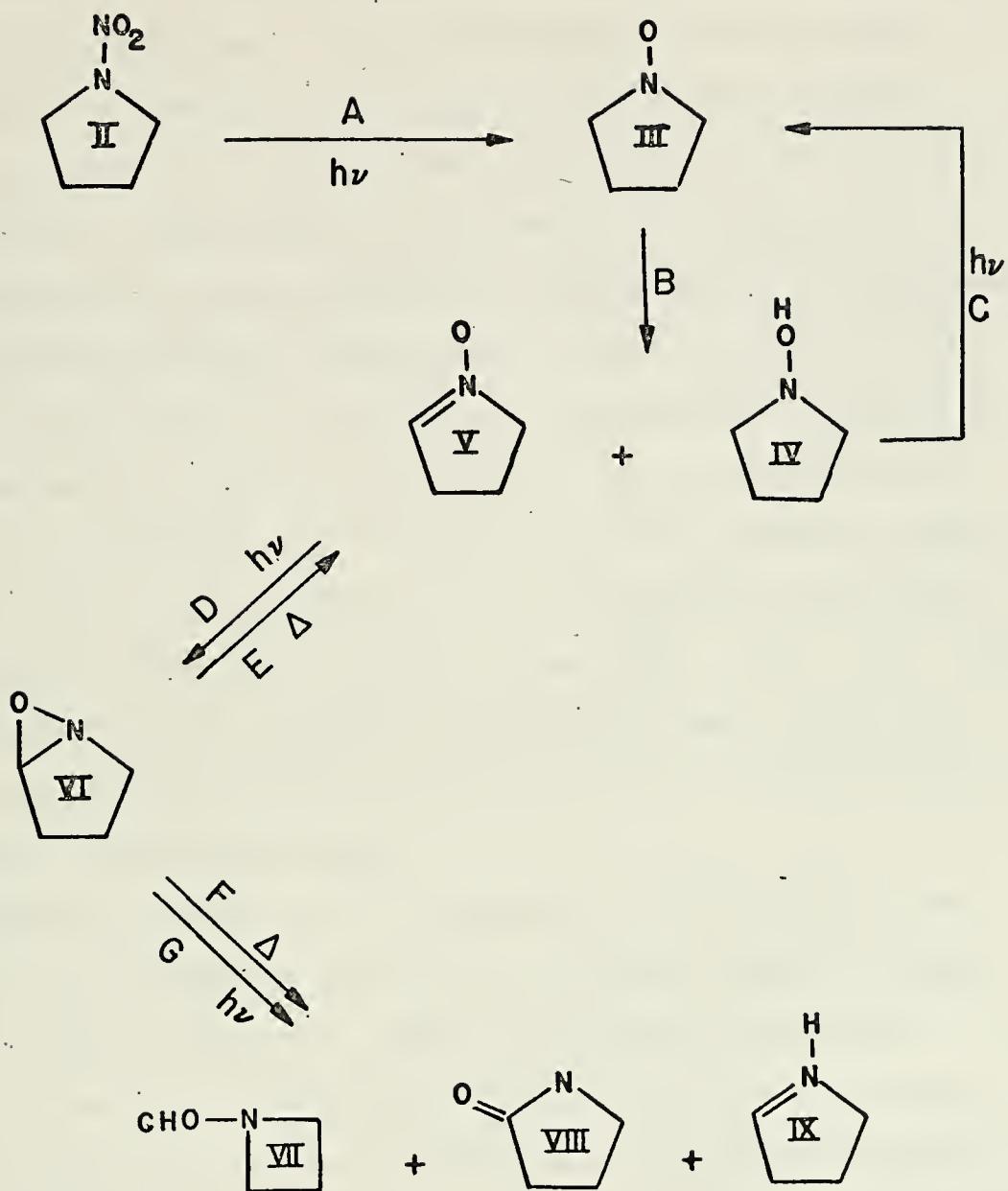


Figure 4. Proposed Mechanism for the Photochemical Decomposition of 1-Nitropyrrolidine

hydroxylamines [15, 16], and 1-hydroxypyrrolidine (IV) in particular [19, 20], to give the corresponding nitroxide radicals (Step C) is also well known. Step C acts to regenerate the nitroxide radical (III) from the hydroxylamine (IV).

Todd and Lamchen [21, 22] have found that irradiation of various substituted 1-pyrroline-1-oxides yield the corresponding bicyclic oxaziridines. From the work of Emmons [23] it is apparent that the stability of these bicyclic oxaziridines is enhanced by methyl substitution in the 5 position. Consistent with this is the difficulty encountered by both Todd and Lamchen [21, 22] in the isolation of the corresponding bicyclic oxaziridine from photolysis of the 2-methyl-1-pyrroline-1-oxide. The lifetime of the unsubstituted oxaziridine is expected to be on the order of two weeks. Thus, while the oxaziridine (VI) is expected to be formed photochemically from the nitrone (Step D), the chances of its detection and isolation are questionable.

The oxaziridine (VI) may decompose by both thermal and photochemical routes. Emmons [22] detected both the parent nitrone and the isomeric amide from thermal degradation (Steps E and F). While Lamchen [22, 24] has isolated the corresponding pyrroline, pyrrolidone, and N-acetylazetidine from the photochemical degradation, the pyrrolidone is found to be the major product when the oxaziridine is unsubstituted in the 5 position.

III. EXPERIMENTAL

A. INSTRUMENTATION

All melting points were taken on a Fisher-Johns melting point apparatus.

Infrared absorption spectra were determined using a Perkin-Elmer 337 Grating Infrared Spectrophotometer, unless otherwise specified. Peaks are reported in wave numbers, and are followed by two sets of letters which describe the peak. The first set refers to the intensity where s, m, and w denote strong, medium, and weak. The second set refers to the general shape where s indicates sharp, and b indicates broad. A prefix of "v" means very. Spectra were calibrated with known peaks of polystyrene at 1601 and 1069 cm^{-1} . Liquids were run as neat samples between silver chloride plates unless otherwise specified. Solids were examined as KBr pellets.

Ultraviolet spectra were obtained on a Beckman DK-1A Ultraviolet Spectrophotometer. Unless otherwise specified, the samples were examined in 1 cm quartz cells.

Nuclear magnetic resonance spectra were determined at 30°C with a Hitachi Perkin-Elmer R-20A High Resolution NMR Spectrophotometer. Chemical shifts are reported relative to TMS, which was used as an external standard.

The gas chromatograms were determined on a Bendix Series 2200 Laboratory Chromatograph. An 8' x $1/8$ " column of 20% SE-30 on Chromabsorb W was used for all analyses. The inlet

and detector temperatures were 175°C unless otherwise specified. The carrier gas was helium, and the flame ionization detector was used unless specified differently. Flow rates were as follows:

helium	50 ml/min
hydrogen	40 ml/min
air	1.8 cfm

The instrument was equipped with an automatic temperature programmer which allowed control of temperature as a function of time. The two most frequently used temperature programs were as follows:

Program 1	Temp 1	45°C
	Time 1	4 min
	Rate 1	25°C/min
	Temp 2	60°C
	Time 2	5 min
	Rate 2	8°C/min
	Temp 3	140°C
	Time 3	8 min
	Cool	9 min
Program 2	Temp 1	70°C
	Time 1	5 min
	Rate 1	5°C/min
	Temp 2	130°C
	Time 2	0 min
	Rate 2	30°C/min
	Temp 3	200°C
	Time 3	2 min
	Cool	9 min

Retention times are reported as ratios relative to 1-nitropyrrolidine, which had a retention time of 18 minutes.

The source of all photolyses was a Christie 200 W high pressure arc operated at 110 V. The samples were at a distance of one meter from the source. The beam was focused

through quartz optics onto an area just large enough to irradiate the entire sample.

B. SOLVENTS

1. Tetrahydrofuran [25]

Lithium aluminum hydride (3 g) was added in small portions to a well stirred solution of tetrahydrofuran (2 l). Small samples were withdrawn and tested for activity with water. When vigorous evolution of hydrogen occurred, an additional 2 g of the hydride was added. The solvent was distilled away from the hydride at atmospheric pressure.

2. Hexane [26]

a. Hexane (1.5 l, Matheson, Coleman, and Bell reagent grade) was washed with a mixture of 75 ml of concentrated sulfuric acid and 25 ml of concentrated nitric acid. The hexane was then washed with water to remove any acid remaining, dried over sodium sulfate, and distilled away from potassium permanganate through an 18 inch Vigreux column (77.5-79.5°C). The distillate was passed through a column $\frac{3}{4}$ inch in diameter packed with 50 g of neutral activated aluminum oxide to remove any aromatic impurities present. The purified solvent had an ultraviolet cut-off at 217 nm measured in a 1 cm cell using distilled water as a reference, and was found suitable for use in gas chromatographic analysis.

b. Chromatoquality hexane, manufactured by Matheson, Coleman, and Bell was used without additional purification.

3. Cyclohexane

Spectroquality cyclohexane, obtained commercially from Matheson, Coleman, and Bell, was found suitable for use without additional purification.

4. Isopentane (2-methyl-Butane)

Isopentane (Baker grade) was obtained commercially from the J. T. Baker Company and was found suitable for use without additional purification. The ultraviolet cut-off was at 206 nm measured in a 1 cm cell with distilled water as a reference.

C. SYNTHESIS

1. 1-Formylpyrrolidine [27]

Freshly distilled pyrrolidine (51.1 g) was placed into a 250 ml round-bottom flask equipped with a condenser and dropping funnel. Over a period of 40 minutes, formic acid (32 ml) was added dropwise through the condenser into the reaction vessel, which was stirred continuously at 0°C. This resulted in the formation of a white cloud in the condenser. The reaction was set under reflux for 1.5 hours. After being cooled to room temperature, the reaction mixture was extracted with three 75 ml portions of methylene chloride, which were in turn combined, washed with 2N sodium hydroxide, and dried over sodium sulfate. Following removal of solvent on the rotary evaporator, a yellow oil remained. Distillation at 98.8-99.5°C/13 mm (lit. 98°C/14min [28]) gave 47 g of a clear liquid. This was a 65% yield.

NMR (CCl₄)

singlet	8.05
multiplet	3.35
multiplet	1.9
(lit. 3.8 and 2.2 [29])	

IR

2970 (s-vb)	1410 (s-s)	1185 (w-b)	925 (w-b)
2870 (s-b)	1380 (s-s)	1160 (w-b)	910 (m-s)
1660 (vs-s)	1330 (m-s)	1115 (w-b)	870 (m-b)
1490 (m-s)	1295 (w-s)	1027 (m-s)	812 (m-s)
1460 (m-s)	1245 (w-b)	965 (m-s)	705 (m-s)

2. 1-Nitropyrrolidine [27]

Trifluoroacetic acid (127 ml) and acetic anhydride (127 ml) were combined in a three-neck one liter round bottom flask equipped with two dropping funnels. The flask was placed in a salted-ice bath. Red fuming nitric acid (90 ml) was added to the well-stirred solution over a period of two hours. To this orange solution, 1-formylpyrrolidine was added dropwise over a 40 minute interval, and the stirring continued for an additional two hours. The reaction vessel was then removed from the ice bath and allowed to stand for an additional hour at 30°C. This orange solution was poured carefully onto 400 ml of crushed ice. The resulting blue-green solution was extracted with six 50 ml portions of methylene chloride, which were then combined, washed with water, and dried over sodium sulfate. Evaporation of the solvent on a rotary evaporator gave a light yellow oil, which was pumped on for 20 minutes to remove remaining solvent. This oil was taken up in a minimum of warm hexane-ether (3:1) from which

the product was crystallized. The long needle-like crystals were collected, and pumped on to remove remaining solvent. Subsequently, 28.5 g of the crude product was recovered, which was a 60.9% yield.

This crude product was again taken up in warm hexane-ether (3:1), cooled slowly to liquid nitrogen temperature, and the resulting crystals collected. Final purification was obtained by dissolving these crystals in the same warm solvent mixture, and allowing crystallization to occur undisturbed, overnight in a freezer. In this manner, 18 g of pure material was obtained, melting at 58.0-58.8°C (lit. 58-59°C [27]).

NMR (CCl_4)

multiplet	2.0
multiplet	3.7

IR

3010 (s-s)	1310 (s-s)	1022 (s-s)	760 (vs-s)
2970 (s-s)	1220 (s-s)	970 (s-s)	708 (w-s)
2900 (s-s)	1186 (m-s)	921 (m-s)	605 (s-s)
1490 (s-s)	1165 (w-s)	905 (s-s)	565 (s-s)
1460 (s-s)	1130 (m-s)	850 (s-s)	430 (s-s)
1380 (s-b)			

UV

$$\lambda_{max} (EtOH) = 240 \text{ nm} \quad \log t = 3.9$$

3. Potassium Salt of Pyrrole

A five liter three-neck flask equipped with a dry ice-acetone condenser, straight condenser, and magnetic stirrer was filled half way with liquid ammonia. To this was added 100 mg of ferrous ammonium sulfate. Potassium (49.8 g; 1.27 mole) was added slowly in 5 to 15 g pieces to the well stirred

solution, causing formation of an intense blue color. Freshly distilled pyrrole (85.6 g: 1.28 mole) was added dropwise over a 20 minute period. The reaction mixture became almost clear, having a slight mustard color. Ether (500 ml) was added, and the flask then was immersed in a warm water bath to evaporate the liquid ammonia. The solid remaining was collected, and pumped on to remove adhering solvent. This procedure was performed open to the atmosphere as quickly as possible to minimize absorption of water. The final product was 122 g (91.3% yield) of a fine, dry, almost white solid, which was stored in a tightly sealed jar in a dessicator.

4. 1-Ethylpyrrole

The potassium derivative of pyrrole anion (30 g: 0.28 mole) and tetrahydrofuran (300 ml) were combined in a two liter round bottom flask equipped with a reflux condenser, addition funnel, drying tube and magnetic stirrer. To this was added freshly distilled ethyl iodide (50 g: 0.32 mole) dropwise over a period of 20 minutes. The reaction mixture was set under reflux for 50 hours, and then allowed to cool slowly to room temperature.

The resulting yellow liquid was filtered away from the tan solid, and placed on the rotary evaporator where the volume was reduced to approximately 20 ml. Distillation at 65-68°C/98 mm (lit. 129-130/762 mm [30]) gave 13.5 g (51% yield) of a crude product. This clear liquid was found to contain considerable (15-20%) pyrrole, probably formed as a result of the base catalysed elimination of HI from ethyl iodide to give ethylene. Purification was possible by repetitive

extraction with water to remove pyrrole, although this resulted in loss of much of the desired product.

NMR (acetone d₆)

triplet	6.8 (2)
triplet	6.2 (2)
quartet	4.0 (2)
triplet	1.55 (3)

IR

3170 (m-s)	1500 (m-s)	1300 (w-s)	987 (m-s)
3140 (m-s)	1460 (m-s)	1279 (s-b)	937 (m-s)
3005 (s-s)	1440 (m-s)	1229 (w-b)	879 (w-b)
2970 (m-s)	1380 (m-s)	1118 (m-b)	721 (vs-b)
2905 (m-b)	1350 (m-s)	1089 (s-s)	649 (m-s)
1530 (s-s)		1059 (s-s)	614 (s-s)

5. 1-n-Pentylpyrrole [31]

In a two liter three-neck round bottom flask equipped with a condenser, dropping funnel, drying tube, and magnetic stirrer, 50 g (0.476 mole) of the potassium salt of pyrrole was combined with 900 ml of tetrahydrofuran. n-Pentylbromide (76.0 g: 0.503 mole) dissolved in 100 ml of tetrahydrofuran was added dropwise to the reaction mixture over a period of 30 minutes. The reaction was set under reflux for 90 hours, at the completion of which it had a white, milky appearance. Following removal of the white solid by suction filtration, the reaction volume was reduced to 100 ml on the rotary evaporator. The remaining yellow liquid was distilled at 104-107°C/45 mm (lit. 95-96°C/28 mm [32]) yielding 52 g (79.8% yield) of a clear liquid. No pyrrole was found to be present.

NMR (acetone-d₆)

triplet	6.82 (2)
triplet	6.20 (2)
triplet	4.05 (2)
multiplet	1.5 (9)

IR

3110 (m-s)	1395 (w-s)	1062 (s-s)	815 (m-s)
2960 (s-b)	1360 (m-b)	1030 (vw-b)	720 (vs-b)
2880 (s-b)	1280 (s-b)	990 (vw-b)	650 (m-s)
1530 (w-b)	1220 (w-b)	966 (s-s)	455 (m-b)
1455 (s-b)	1087 (s-s)		

6. 1-Ethylpyrrolidine [33]

1-Ethylpyrrole (12 g: 0.126 mole) was placed in a 250 ml round bottom flask along with 30 ml of acetic acid. To this was added 0.8 g of PtO₂ as a slurry in 10 ml of acetic acid. The mixture was stirred vigorously under a hydrogen atmosphere until the rate of gas absorption became extremely slow (25 hours). Ether (100 ml) was then added, and the reaction mixture was filtered to remove remaining catalyst. The filtrate was cooled in an ice bath, and made basic by the addition (slow) of 25% sodium hydroxide. Enough water was added to dissolve the white salt which had formed. The organic phase was separated, and the remaining aqueous phase was extracted with two 50 ml portions of ether. All organic phases were combined and dried over sodium sulfate. The total volume was reduced to 15 ml by distillation of ether through an 18 inch vigreux column. Short path distillation gave 2.8 g (22.4% yield) of a clear liquid at 90-101°C/760 mm (lit. 104°C/760 mm [33]). Gas chromatography indicated the purity to be greater than 90%. The most significant impurity was unreacted

1-ethylpyrrole. The following physical constants were collected:

Picrate 184-186.5°C (lit. 184-186°C [33])

NMR (acetone-d₆)

multiplet	2.7 (6)
multiplet	2.0 (4)
triplet	1.32 (3)

IR

2970 (s-b)	1320 (m-s)	1100 (s-s)	905 (vw-s)
2880 (m-b)	1280 (m-b)	1086 (w-s)	865 (m-b)
2780 (s-b)	1235 (w-b)	1060 (m-s)	720 (s-b)
1505 (w-s)	1200 (m-b)	965 (w-b)	655 (vw-b)
1460 (m-b)	1170 (m-b)	950 (w-b)	615 (w-b)
1390 (m-s)	1155 (m-b)	935 (vw-s)	
1350 (m-s)			

7. 1-n-Pentylpyrrolidine

1-n-Pentylpyrrole (21 g: 0.153 mole) was placed in a 250 ml flask along with 40 ml of acetic acid. To this was added 1.1 g of platinum oxide in a slurry of 20 ml of acetic acid. The reaction mixture was stirred vigorously under a hydrogen atmosphere until gas absorption had completely ceased (24 hours). Ether (100 ml) was added and the reaction mixture was filtered to remove remaining catalyst. The resulting solution was cooled in an ice bath and made basic by the addition (slow) of 25% sodium hydroxide solution. The organic layer was separated and the aqueous phase extracted with two 75 ml portions of ether. All organic phases were combined, dried over sodium sulfate, and placed on the rotary evaporator. Distillation at 85-88°C/33 mm (lit. 81-82°C/28 mm [32]) gave 14.7 g (68.0% yield) of a clear liquid. Gas chromatography indicated the product purity to be greater than 99%.

Picrate 118-119°C (lit. 117.5-118°C [32])

NMR	(acetone-d ₆)
	multiplet 2.7 (6)
	multiplet 1.7 (13)

IR

2950	(vs-b)	1290	(m-b)	1108	(m-s)	905	(m-s)
2890	(s-b)	1236	(m-b)	1091	(m-s)	873	(m-b)
2795	(s-b)	1218	(m-b)	1028	(w-vb)	773	(vw-b)
1470	(s-s)	1203	(w-b)	1003	(w-vb)	728	(m-b)
1380	(m-s)	1192	(w-b)	953	(w-vb)	623	(w-vb)
1350	(s-s)	1153	(s-b)	928	(w-vb)	583	(w-vb)

8. 1-Ethylpyrrolidine-1-Oxide [34]

1-Ethylpyrrolidine (3.6 g: 0.0364 mole) was placed in a 50 ml round bottom flask. To this was added 7.8 g (0.073 mole) of 30% hydrogen peroxide with constant stirring. Two phases were initially present, which mixed slowly with slight evolution of heat. A condenser was attached to the reaction vessel and the mixture stirred in a water bath at 60°C for 11 hours. The flask was then cooled in an ice bath, and platinum black added to remove excess hydrogen peroxide. After the reaction had been allowed to stand at room temperature for an additional hour, the yellow aqueous solution was filtered away from the platinum black. Removal of water on the rotary evaporator under 20 mm pressure using a 60°C water bath left behind a viscous yellow oil.

9. 1-n-Pentylpyrrolidine-1-Oxide

Into a 100 ml round bottom flask was placed 10.5 g (0.0745 mole) of 1-n-pentylpyrrolidine. To this was added slowly, with stirring, 20 g (0.18 mole) of hydrogen peroxide (30%). The reaction mixture was then stirred at 55°C for

20 hours. The two phases initially present mixed slowly over a period of several hours, giving a light yellow solution. After three hours had elapsed, a spot test with phenolphthalein [35, 36] generated a pink color, due to the presence of the original amine. However, at the completion of the 20 hour period, no pink color was observed, indicating that the reaction had gone to completion.

Excess hydrogen peroxide was decomposed by the addition of platinum black (0.2 g). The reaction mixture was then allowed to stir for an additional hour at 60°C. A spot test with aqueous potassium iodide did not give a dark brown color, thus indicating the absence of remaining hydrogen peroxide.

Filtration gave a light yellow solution. As much water as possible was removed on the rotary evaporator, under a pressure of 10 mm using a water bath at 55°C, yielding 12.3 g (11.7 theoretical) of a viscous yellow oil.

Picrate mp. 85-87°C

10. 1-Hydroxypyrrolidine

A 100 ml side arm flask was equipped with a dropping funnel. To this was attached a condenser, cooled with ice water, a 100 ml collection vessel cooled in a salted ice bath, and a trap at liquid nitrogen temperature. The side arm flask was immersed in an oil bath at 185°C, and the system was evacuated to 30 mm.

1-n-Pentylpyrrolidine-1-oxide (11.7 g, p. 27) was added dropwise into the pyrolysis flask over a period of 1

hour. Pyrolysis occurred immediately, and little or no reflux of products back into the heated flask occurred. At the completion of the pyrolysis 8.2 g of a brown solution was in the collection vessel, 2.0 g of a clear liquid was in the liquid nitrogen trap, and 0.5 g of a black tar remained in the pyrolysis flask.

Gas chromatographic analysis indicated that the material in the collection flask was a mixture of two components having the retention times of 1-hydroxypyrrolidine (30%) and 1-n-pentylpyrrolidine (70%). Distillation yielded a clear liquid with an IR very similar to that of 1-n-pentylpyrrolidine and a picrate which melted at 115-117°C. The clear liquid (believed to be 1-pentene) collected in the liquid nitrogen trap was extremely volatile, and contained no higher boiling components as indicated by gas chromatography. This indicates that the product in the collection flask contained 30.5% of the desired product, corresponding to a yield of 40.5%.

Purification was obtained by preparative gas chromatography.

IR			
3320 (vs-vb)	1290 (m-b)	1030 (s-s)	874 (m-s)
2990 (s-b)	1220 (m-b)	1010 (m-b)	808 (s-b)
2870 (s-b)	1196 (m-s)	950 (w-b)	555 (m-s)
1460 (s-b)	1125 (m-s)	930 (s-s)	465 (m-b)
1340 (m-s)		895 (m-s)	420 (m-b)

11. Pyrolysis of 1-Ethylpyrrolidine-1-Oxide [34]

1-Ethylpyrrolidine 1-oxide (from p. 27) was placed in a 50 ml flask equipped with a distillation unit, a

collection flask, and an oil bath. The temperature of the bath bath was raised slowly to 140°C. Soon after the pyrolysis began, a vigorous bump occurred, leaving behind only a dark viscous residue and black solid deposit.

12. 1-Hydroxypyrrolidine [37]

A two liter flask containing 500 ml of tetrahydrofuran was equipped with a condenser, dropping funnel, and drying tube. Lithium aluminum hydride (6.5 g: 0.1714 mole) was added very slowly. A solution of N-hydroxysuccinimide (10 g: 0.087 mole) in 400 ml of tetrahydrofuran was added dropwise over a period of one hour, and the reaction left under reflux for an additional 24 hours. The reaction was allowed to cool to room temperature, and excess lithium aluminum hydride destroyed by the addition (slow) of wet tetrahydrofuran (100 ml/25% water). The mixture was filtered and the resulting yellow solution placed on the rotary evaporator to remove as much solvent as possible. This was extracted with two 50 ml portions of ether, which were in turn combined, and dried over sodium sulfate. After removal of ether on the rotary evaporator, 1.2 g (15.8% yield) of product was distilled at 65°C/6 mm (lit. 67-68°C/14 mm). Gas chromatography indicated that the product was 92% pure, and NMR indicated the presence of a considerable amount of water. Final purification was obtained by preparative gas chromatography.

NMR	(acetone-d ₆)
	multiplet
	3.2
	multiplet
	2.1
	multiplet
	2.4

IR

(Identical to that documented on p. 29).

D. PHOTOLYSIS

1. Photolysis in Hexane

a. 1-Nitropyrrolidine (8.08×10^{-4} M)

The photolysis of an 8.08×10^{-4} M solution of 1-nitropyrrolidine in hexane (MCB-chromatoquality) was examined using gas chromatography and ultraviolet absorption spectroscopy. Samples were irradiated in 1 mm quartz cells for given time periods. The cells were then transferred to the ultraviolet spectrophotometer where the spectra were recorded. Following this, the liquid samples were injected into the gas chromatography unit under the following conditions:

sample size	80 microliters
attenuation	10 x 20
column temperature	program 1

During the first two minutes of irradiation a fine white cloud appeared, and the solution yellowed slightly. Four new peaks (B, C, D, E) became apparent in the gas chromatogram, having retention times of 0.94, 0.80, 0.70, and 0.67 relative to 1-nitropyrrolidine (A). Due to the programming scheme, the injection size, and the boiling point of the solvent, peaks with relative retention times less than 0.27 were hidden in the solvent trail. Detection of small product peaks with retention times less than 0.47 was difficult due to the solvent impurities which were present. Photolysis of the pure solvent gave no new peaks in the gas chromatogram, indicating that the observed products (B, C, D, E) were not due

to the solvent impurities. In addition, the results were reproducible using a solution of the nitramine (at the same concentration) in hexane as purified on p. 19. The results are summarized in Figure 5, and in Table II below.

TABLE II

PHOTOLYSIS OF 1-NITROPYRROLIDINE
 $(8.08 \times 10^{-4} \text{ M})$ IN HEXANE:
 G.C. ANALYSIS OF PRODUCT COMPOSITION

Time of Irradiation	Area ^a Under Peaks				
	A ^b (1.00 ^{c,d})	B (0.94)	C (0.80)	D (0.70)	E (0.67)
0 minutes	33.50	0.00	0.00	0.00	0.00
2 minutes	-	3.15	0.00	0.43	0.35
5 minutes	10.45	5.60	0.28	1.10	1.12
10 minutes	6.80	9.65	0.57	2.45	2.59
15 minutes	3.94	5.70	0.91	3.10	3.29
20 minutes	1.60	1.54	1.05	3.15	2.93
30 minutes	0.00	0.00	1.12	4.18	3.94
70 minutes	0.00	0.00	1.48	4.12	4.00

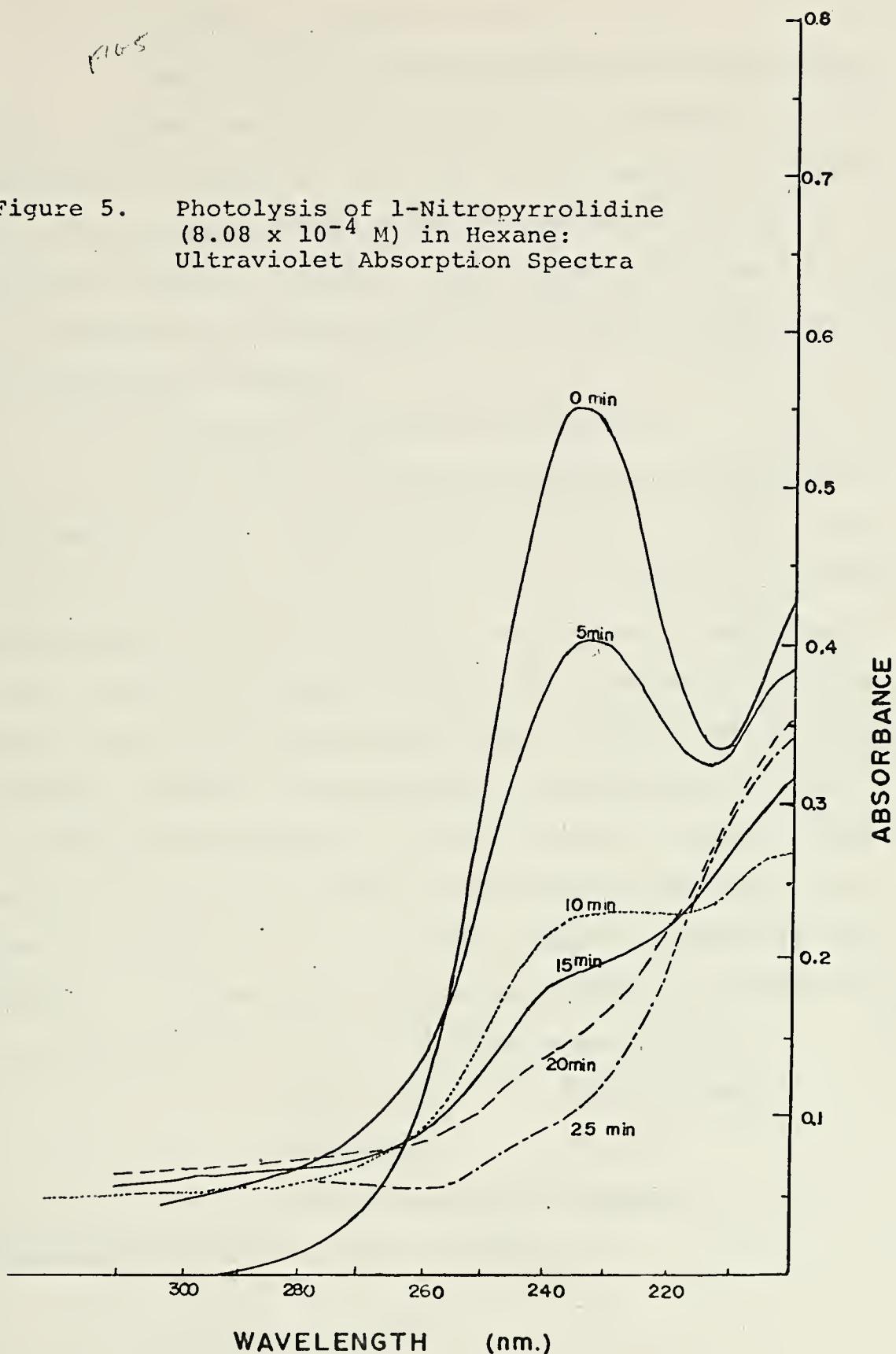
^a Areas are in square centimeters and were calculated as the product of height and half-width.

^b Peak A corresponds to 1-nitropyrrolidine.

^c Numbers given in parentheses are retention times and are reported relative to 1-nitropyrrolidine, with temperature program 1 used for analysis.

^d Peaks with retention times less than 0.27 were hidden in the solvent trail. Detection of small peaks with retention times less than 0.47 was difficult.

PL 65
Figure 5. Photolysis of L-Nitropyrrolidine
(8.08×10^{-4} M) in Hexane:
Ultraviolet Absorption Spectra



b. 1-Nitropyrrolidine (8.08×10^{-5} M)

The above solution (prepared with MCB-chromato-quality hexane) was placed in a 1 cm quartz cuvette and irradiated for a period of two hours. The sample was withdrawn periodically during the irradiation, and the ultraviolet absorption spectrum recorded. The results are shown in Figure 6. Throughout the entire period, the solution remained clear and colorless to the eye.

c. 1-Nitropyrrolidine (1.0×10^{-2} M)

The above solution was prepared with hexane as purified on p. 19. The photolysis was run in a quartz windowed cell, having a capacity of 16 ml. The quartz windows were circular, 10 cm in diameter, and the path length was 2 cm. The solution was photolysed for a period of 17 hours. After 3 hours, the solution had become cloudy, and gas chromatography indicated the presence of components very similar to those observed above (C, D, E). After 17 hours of irradiation, a red oil had formed on the sides of the cell, and products similar to B, C, D, and E observed previously were present. The supernatant liquid was removed and analysed by gas chromatography under the following conditions:

sample size	8 microliters
attenuation	10 x 10
column temperature program	2

The results are given below in Table III.

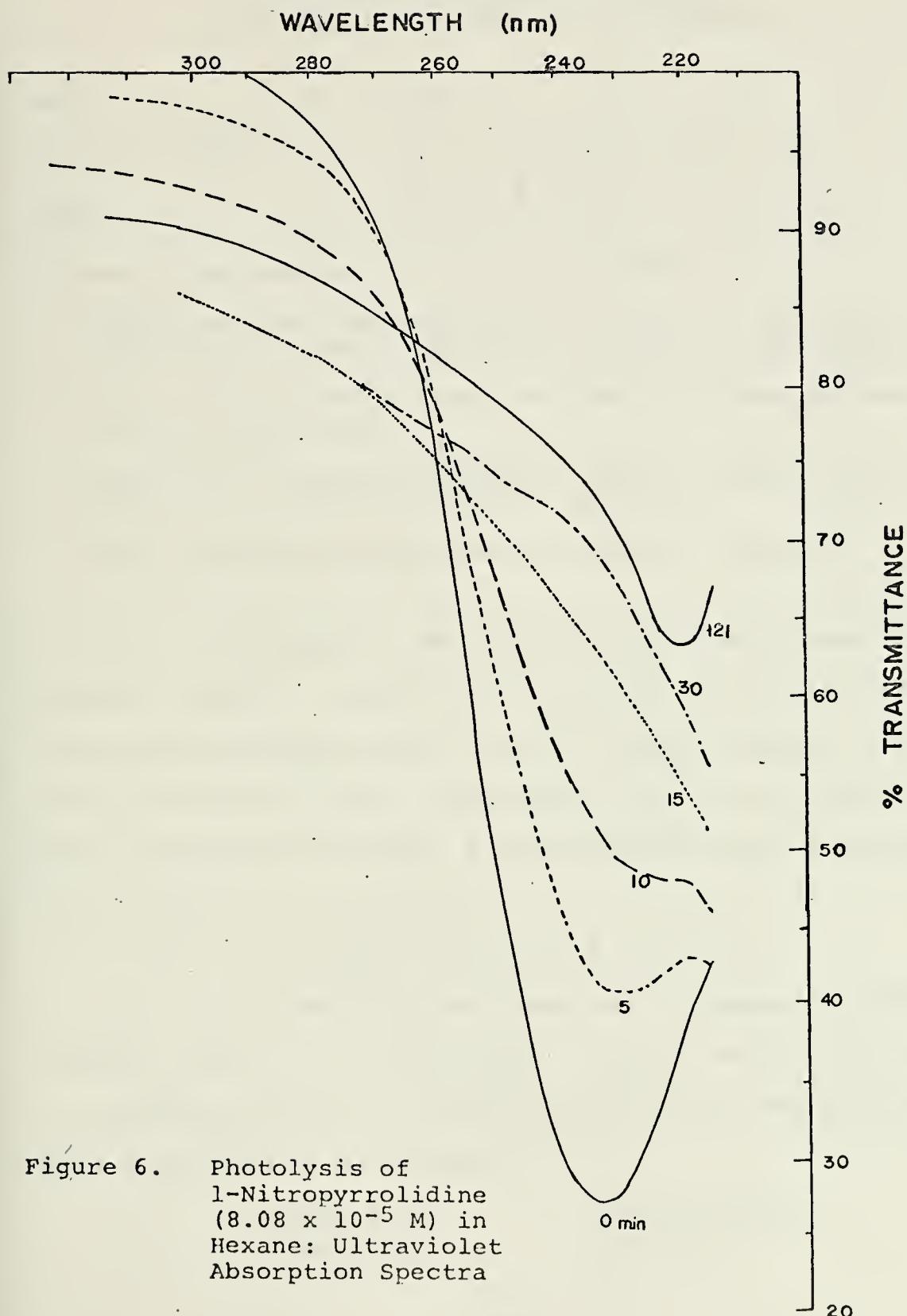


Figure 6. Photolysis of 1-Nitropyrrolidine (8.08×10^{-5} M) in Hexane: Ultraviolet Absorption Spectra

TABLE III
PHOTOLYSIS OF 1-NITROPYRROLIDINE
(1×10^{-2}) IN HEXANE (17 HOURS):
G.C. ANALYSIS OF PRODUCT COMPOSITION

Peak	A ^a	B	C	D	E
Retention Time ^{b,c}	1.00	0.90	0.64	0.52	0.49
Area ^d	>23 ^e	9.50	1.53	2.76	3.12

^a Peak A corresponds to 1-nitropyrrolidine.

^b Retention times are reported relative to 1-nitropyrrolidine, with temperature program 2 used for analysis.

^c Peaks with retention times less than 0.27 were hidden in the solvent trail.

^d Areas are in square centimeters and were calculated as the product of height and half-width.

^e Exact determination unknown as peak was off scale.

The red oil remaining in the photolysis cell was dissolved in absolute ethanol. Injection into the G.C. at column temperatures ranging between 80°C and 140°C gave no peaks. Injections at elevated column temperature (200°C) gave a broad peak which appeared between 4 and 20 minutes, quite possibly due to product decomposition.

d. 1-Hydroxypyrrrolidine (1.0×10^{-3} M)

The photolysis was examined in hexane (chromato-quality) using gas chromatography. Samples were irradiated in 1 mm quartz cells for varying time periods, and analyzed under the following conditions:

sample size	80 microliters
attenuation	10 x 50

temperature program	Temp 1	45°C
	Time 1	10 min
	Rate 1	5 deg/min
	Temp 2	80°C
	Time 2	0 min
	Rate 2	10 deg/min
	Temp 3	140°C
	Time 3	2 min
	Cool	

No new products became apparent. The data is summarized in Table IV.

TABLE IV

PHOTOLYSIS OF 1-HYDROXYPYRROLIDINE
 $(1.0 \times 10^{-3} \text{ M})$ IN HEXANE:
 G.C. ANALYSIS OF HYDROXYLAMINE DECOMPOSITION

Time of Irradiation	Area ^{a,b} of Hydroxylamine (0.37) ^c
0 minutes	26.80
5 ^d minutes	16.70
10 minutes	12.62
15 minutes	9.24
20 minutes	5.90
30 minutes	4.90

^a Areas are in square centimeters, and were calculated as the product of height and half-width.

^b Areas are corrected to uniform sample size at attenuation 10×20 using a solvent impurity as an internal standard.

^c Retention time is reported relative to 1-nitropyrrolidine when analyzed by temperature program 1.

^d Average of two separate measurements.

2. Photolysis in Isopentane

a. 1-Nitropyrrolidine (2.91×10^{-3} M)

The above solution was photolysed in a 1 mm quartz ultraviolet cell for periods up to 60 minutes. Six new peaks became apparent in the gas chromatogram (G, H, I, J, K, L) with retention times of 0.93, 0.78, 0.47, 0.39, 0.29, and 0.19 relative to 1-nitropyrrolidine. The peak at K(0.29) was a composite of several unresolvable peaks. After 60 minutes of irradiation, the starting material and peak G had disappeared, leaving peaks H, I, J, K, and L. In addition, many other small new peaks appeared as background in the gas chromatogram. The conditions for G.C. analyses were as follows:

sample size	100 microliters
attenuation	10 x 50
column temperature	program 1

The photolysis of pure solvent gave no new peaks in the gas chromatogram. The results are summarized in Table V below.

b. 1-Nitropyrrolidine (1.164×10^{-3} M)

The solution was photolysed as described for the above solution for periods of 10 minutes and 40 minutes. After 10 minutes the usual peaks had appeared. After 40 minutes, the starting material and peak G had disappeared, leaving behind the same products as described previously.

c. 1-Nitropyrrolidine (5.82×10^{-4} M)

This solution was photolysed for periods of 10 minutes and 40 minutes in the same manner as described above. Exactly the same behavior was observed.

TABLE V

PHOTOLYSIS OF 1-NITROPYRROLIDINE
 $(2.91 \times 10^{-3} \text{ M})$ IN ISOPETANE:
 G.C. ANALYSIS OF PRODUCT COMPOSITION

		Area ^a Under Peaks		
		0 minutes	15 minutes	60 minutes
A ^d	(1.00)	>23	3.96	0.00
G	(0.93)	0.00	8.10	0.00
H	(0.78)	0.00	0.25	0.72
I	(0.47)	0.00	0.72	0.66
J	(0.39)	0.00	1.68	1.61
K ^e	(0.29)	0.00	<1.00	<1.00
L	(0.19)	0.00	<0.10	<0.10

^a Areas are in square centimeters and were calculated as the product of height and half-width.

^b Retention times are reported relative to 1-nitro-pyrrolidine with temperature program 1 used for analysis.

^c Peaks with retention times less than 0.14 were hidden in the solvent trail.

^d Peak A corresponds to 1-nitro-pyrrolidine.

^e Peak K was a composite of several unresolvable peaks.

d. 1-Hydroxypyrrrolidine ($1.66 \times 10^{-3} \text{ M}$)

The above solution was photolysed in a 1 cm quartz cell for a period of 95 minutes. Analysis before and after irradiation indicated that the hydroxylamine peak had decreased in size by approximately 20%. No new products were visible. The retention time of the hydroxylamine was 0.37

relative to 1-nitropyrrolidine when analyzed using temperature program 1.

3. Photolysis in Cyclohexane Solution

a. 1-Nitropyrrolidine (1×10^{-2} M)

One liter of the above solution was prepared in spectroquality cyclohexane obtained from MCB. A flow system was designed consisting of a photolysis cell, 900 ml glass coil for solution storage, and a metering pump. All connections were made with teflon tubing. The photolysis cell had a path length of 10 cm, with quartz windows at each end, which were circular and 4 cm in diameter. Solution inlet and outlet connections were located at opposite ends of the cell. The cyclohexane solution was pumped from the coil, into the photolysis cell, through the pump, and back into the coil at a rate of $10 \text{ cm}^3/\text{sec}$ for a 20 hour period. The resulting solution was analyzed by gas chromatography, which indicated that only one new major peak (Z) had appeared. Its retention time was 0.76 relative to the starting nitramine when analyzed by temperature program 2, and 0.87 when analyzed by temperature program 1. This large peak was followed by a much smaller peak whose area was only 2.4% of the larger. Photolysis of pure solvent gave no new peaks in the gas chromatogram. Peaks with retention times less than 0.5 were hidden in the solvent peak when analyzed by temperature program 1.

The solution was reduced in volume on the rotary evaporator. Peak Z and the smaller adjacent peak were collected by preparative gas chromatography under the following conditions:

sample size	80 microliters
detector	thermal conductivity
temperature program	Temp 1 85°C Time 1 5 min Rate 1 5 deg/min
	Temp 2 100°C Time 2 0 min Rate 2 30 deg/min
	Temp 3 200°C Time 3 1 min
	Cool 9 min

The clear liquid was collected in a 3 mm glass U-tube immersed in a dry ice-acetone solution. Reinjection of the collected product indicated that only the two original peaks were present, in their original proportions. The IR of this compound determined on a Perkin-Elmer 621 Grating Infrared Spectrophotometer is as follows:

2938 (s-b)	1277 (s-b)	1037 (m-s)	807 (w-s)
2862 (s-b)	1360 (w-b)	1007 (m-s)	757 (m-s)
1622 (s-s)	1238 (w-s)	945 (m-s)	712 (w-s)
1547 (w-b)	1190 (vw-b)	915 (w-s)	695 (m-s)
1455 (m-s)	1157 (w-s)	903 (w-s)	647 (m-s)
*1360 (w-s)	1125 (w-s)	867 (s-b)	537 (s-s)
1320 (m-s)	1090 (vw-s)	844 (m-s)	

* doublet

Approximately 0.05 g of the clear liquid was dissolved in 10 ml of hexane. The ultraviolet absorption spectrum of this solution had a cutoff at 253 nm with a broad absorption trailing out to 330 nm. Successive dilution of this solution indicated there was no ultraviolet absorption maxima at any wavelength greater than 200 nm.

IV. DISCUSSION

A. SYNTHESIS

1-Hydroxypyrrrolidine, a suspected intermediate in the photochemical decomposition of 1-nitropyrrolidine, was synthesized via two independent routes.

1. Method 1: Pyrolysis of Amine Oxides

The pyrolysis of tertiary amine oxides to give dialkyl hydroxylamines and the corresponding olefins is a well known reaction of general synthetic utility [36, 38] usually reported in moderate to high yields. The overall reaction scheme is illustrated in Figure 7. There is substantial evidence that the reaction proceeds by a mechanism involving a planar, five membered cyclic transition state, as shown. Thus a major requirement for the reaction to occur is that the β -alkyl hydrogen atoms be sterically accessible. It accordingly has been shown that heterocyclic amines whose hydrogens are sterically inaccessible do not undergo ring opening [39]. This should, therefore, be an excellent synthetic route to heterocyclic hydroxylamines from the corresponding tertiary amines. With N-ethylpiperidine, a 42% of yield of N-hydroxypiperidine was recovered [40, 41]. Thesing [34] using N-ethylpyrrolidine, obtained a 53% yield of N-hydroxypyrrrolidine.

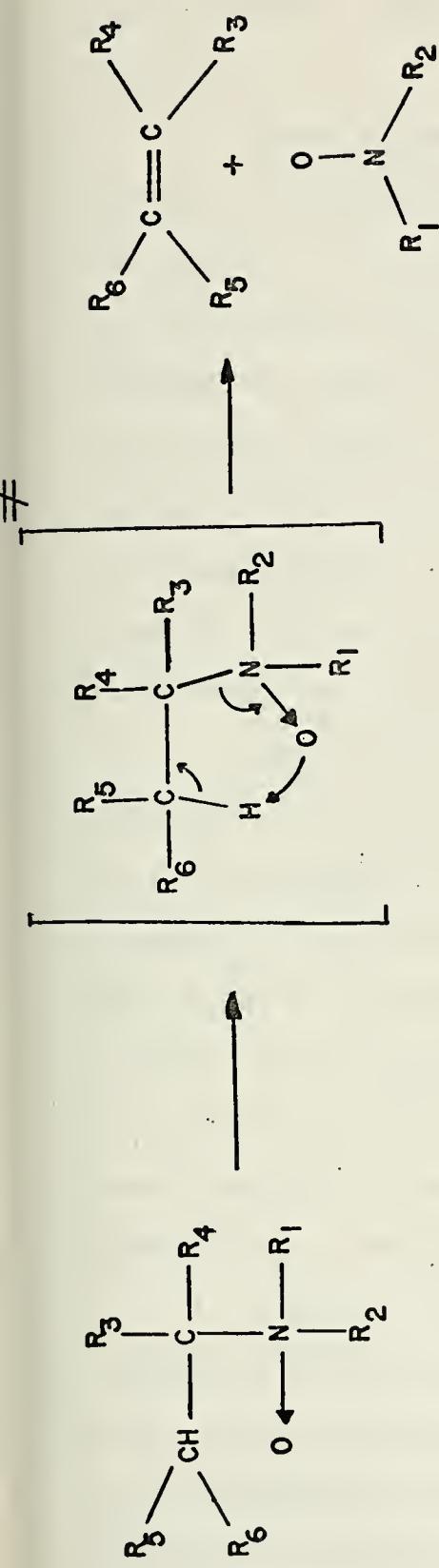


Figure 7. Mechanism for Pyrolysis of Amine Oxides

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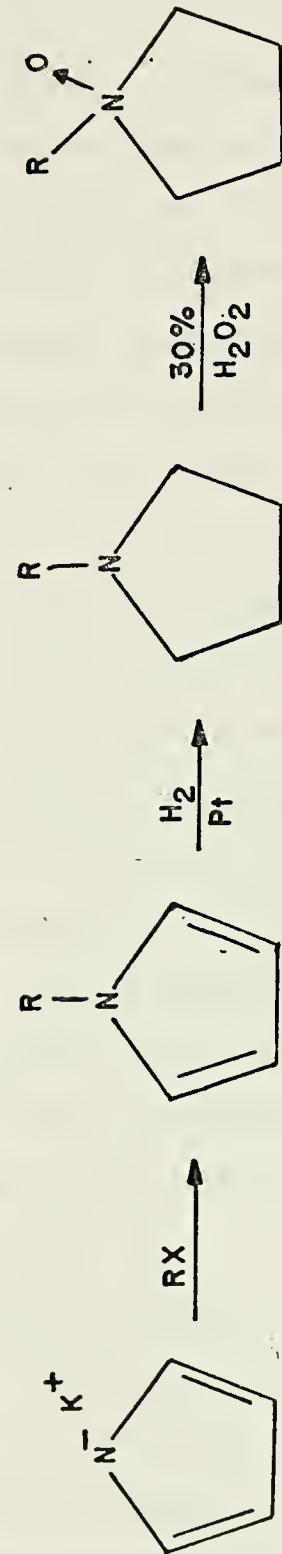


Figure 8. Synthetic Route to 1-Alkylpyrrolidine-1-Oxides

It was decided to attempt this route using N-alkyl-pyrrolidines. The general synthetic route is shown in Figure 8.

First attempts were from N-ethylpyrrolidine. N-ethyl-pyrrole was synthesized using ethyl iodide and potassium salt of pyrrole. Only 51% of a crude product found to contain 15-20% pyrrole was recovered. The pyrrole was presumably formed as a result of the base catalysed elimination of HI from ethyl iodide. The hydrogenation reaction went in 22% yield, with no other products isolated. While this reaction was documented in the literature [33], no yield was reported. The pyrolysis was attempted twice, each time resulting in a vigorous bump leaving only tar and a black solid deposit.

More success was found, however, using 1-N-pentyl-pyrrolidine. The N-alkylation of pyrrole was accomplished using N-pentylbromide, which gave 79.8% yield of a pure product. The hydrogenation also proceeded well, giving a 68% yield of 1-N-pentylpyrrolidine. Pyrolysis gave a crude product containing the hydroxylamine (30%) and a large amount of the starting amine (70%). This result was unexpected and was apparently previously unreported in the literature. As yet no clear explanation has been found.

2. Method 2: Reduction of N-hydroxysuccinimide with lithium aluminium hydride in ether was previously reported to give the corresponding hydroxylamine in 25% yield [37]. Due to difficulties encountered by previous workers [12], it was decided to attempt the reaction in tetrahydrofuran. The

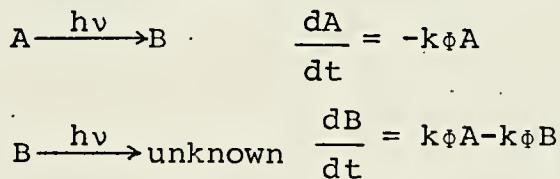
method was moderately successful, giving N-hydroxypyrrrolidine in 15% yield.

B. PHOTOLYSIS

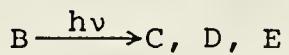
1. Photolysis in Hexane

The photolysis of 1-nitropyrrolidine was examined at three differing concentrations. In the first solution (8.08×10^{-4} M) the gas chromatograms and ultraviolet spectra were recorded as a function of time. Inspection of Figure 6 shows the peak at 235 nm disappearing with no other sharp maxima appearing.

The data in Table I is shown graphically in Figure 9. Peak A is seen to decrease exponentially. A plot of the logarithm of the concentration of A as a function of time gives the straight line shown in Figure 10, with $k_{obs} = 0.0011 \text{ sec}^{-1}$. Peak B is formed immediately upon irradiation, reaches a maximum at ten minutes, and then dies out. Peak B was found to be thermally stable over a period of several days in the dark. The above is consistent with the following scheme:



The origin of peaks C, D, and E seems rather uncertain. Examination of Figure 9 might suggest the following:



However, the other possibility, that C, D, and E are formed directly from A cannot be ruled out.

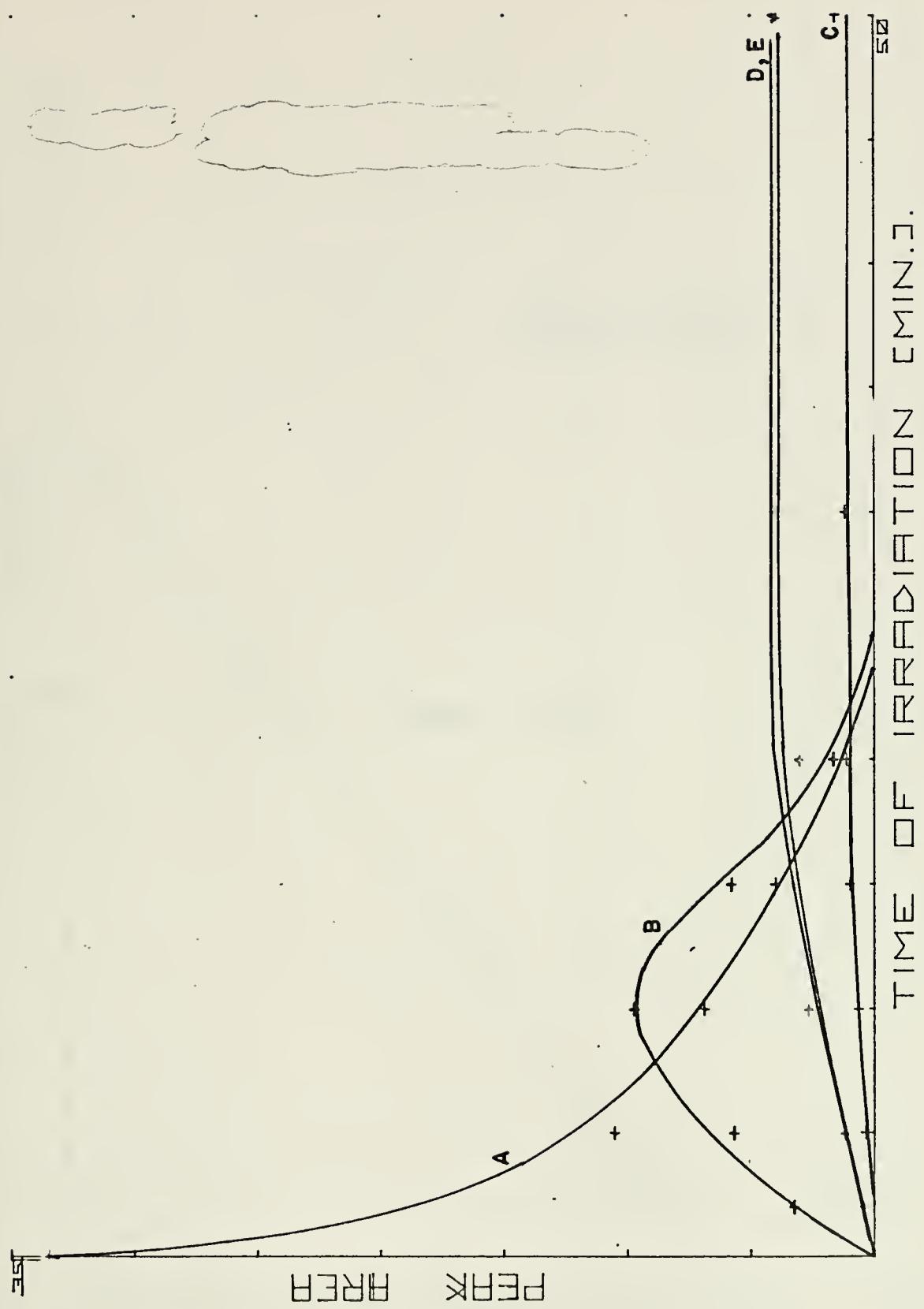
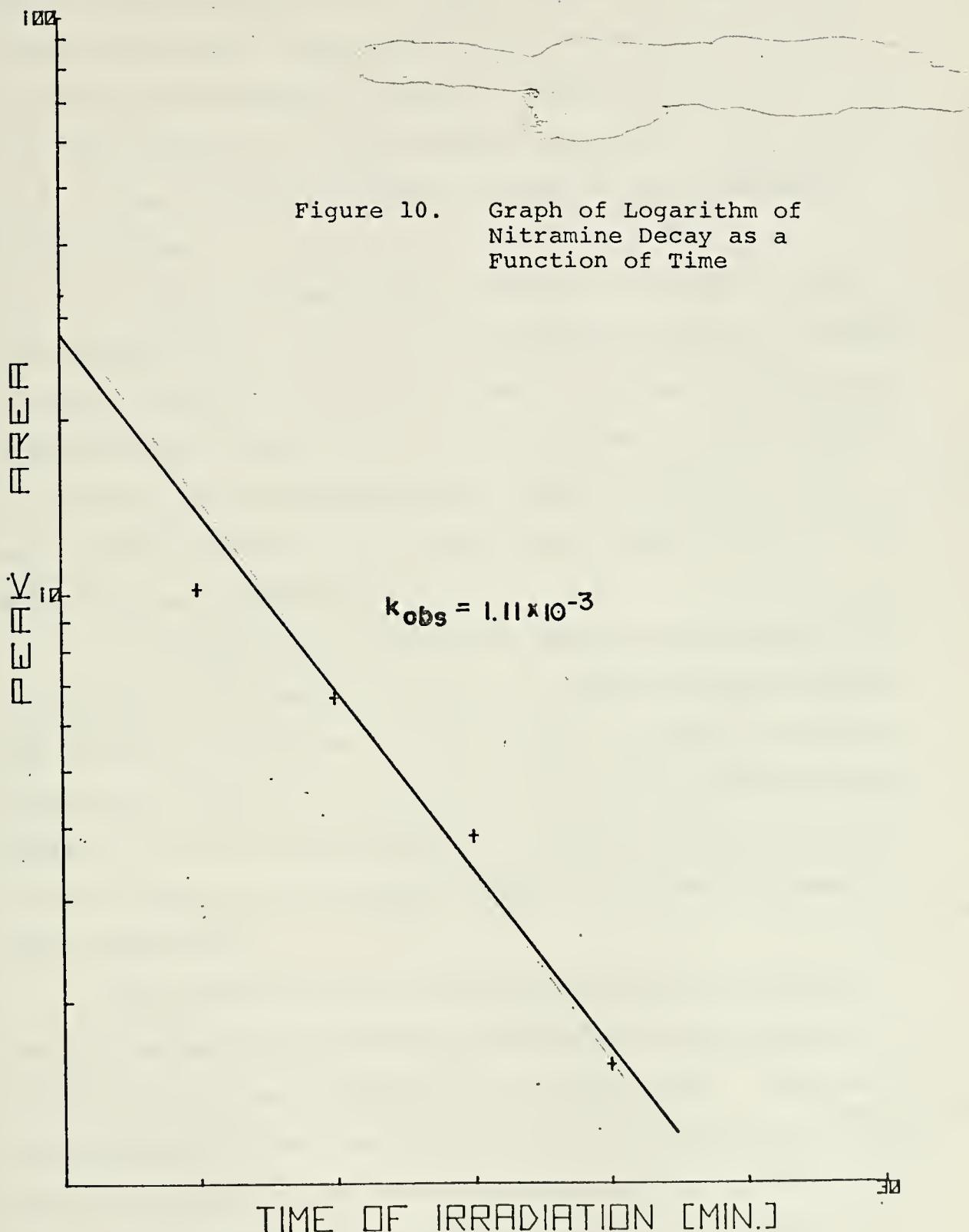
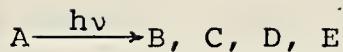


Figure 9. Graph of G.C. Peak Areas as a Function of Irradiation Period





The more concentrated solution (10^{-2} M) of the nitramine was photolysed in an attempt to isolate some of the observed products. After three hours of irradiation peaks C, D, and E were present. After 17 hours of irradiation, all products (peaks B, C, D, and E) were observed. The presence of C, D, and E without B seems to indicate their formation directly from A.

A red oil formed after 17 hours of irradiation and did not correspond to any of the previously observed products. The fact that it registered no peaks in the gas chromatogram suggests that it may be some sort of polymer. Since products C, D, and E are stable in solution under irradiation, it appears that the red oil is formed from either peak B or the parent nitramine directly.

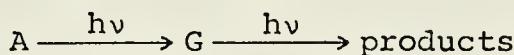
Photolysis of a more dilute solution was examined by ultraviolet spectroscopy and the results are shown in Figure 7. The nitramine absorption at 235 nm again dies out, but upon prolonged irradiation (2 hours) an absorption at 220 nm became apparent. This is most probably a result of the photolysis of one or more of the products formed in the early stages of this irradiation.

The photolysis of 1-hydroxypyrrrolidine in chromatography quality hexane was examined to determine its photochemical stability under the conditions of the photolysis. Samples were photolysed under conditions which were identical to those used previously for the nitramine irradiation. A plot of the log of the peak area of the hydroxylamine as a function of

time is shown in Figure 11. The value of k_{obs} was $5.33 \times 10^{-4} \text{ sec}^{-1}$. The data is not intended to show a rate law for the decomposition of hydroxylamine. The point of interest is that the rate constant for hydroxylamine disappearance is only one-half the rate constant for nitramine decomposition.

2. Photolysis in Isopentane

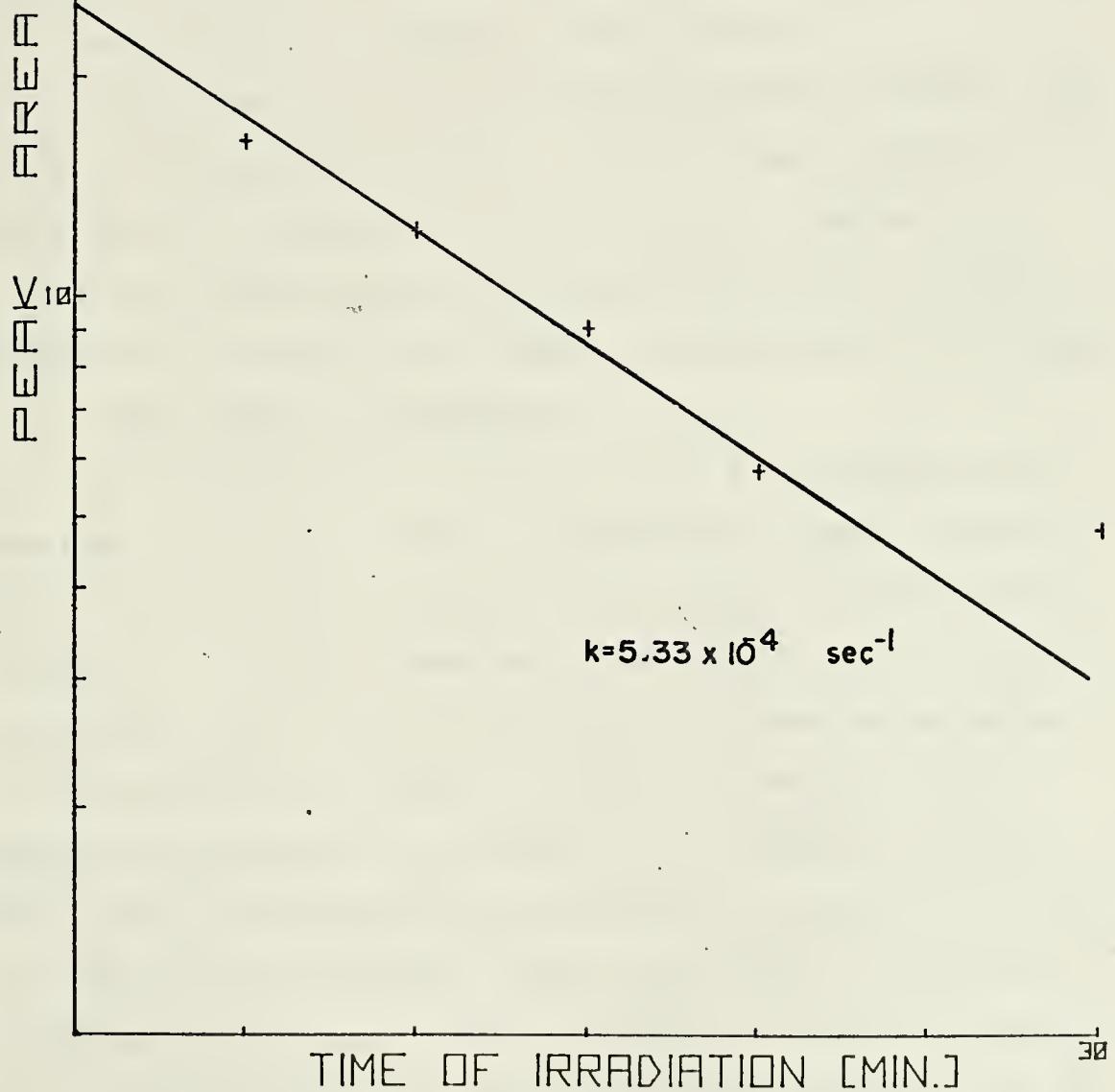
The behavior of three solutions of the nitramine at three differing concentrations was examined using gas chromatography. The behavior was identical for all three. Six new peaks were formed. Peak G was very similar to peak B observed in the hexane solutions, both having the same retention time. In addition, they both had the same behavior, disappearing upon prolonged irradiation. We tentatively conclude that they are identical. Although peak H had a retention time similar to peak C, a definite association was difficult. Peaks I and J were not visible previously in hexane, although they would have been so, if present. Little can be said about peaks K and L as they would have been hidden in the hexane solvent peak. Two of the peaks present in the hexane photolysis, D and E, were definitely not present in the isopentane solutions. Furthermore, H, I, J, K, and L, once formed, did not increase in concentrations appreciably as A and G continued to disappear. By analogy to the photolyses in hexane solutions, we postulate a mechanism as follows:



Since alkane solvents are generally quite inert, we would expect very similar behavior in both hexane and isopentane.



Figure 11. Graph of Logarithm of Hydroxylamine Decay as a Function of Time



The appearance of differing products (C, D, E and H, I, J, K, and L) is difficult to understand. There are several possible explanations:

a. We are observing the reaction of solvent impurities with either oxides of nitrogen or photochemical intermediates formed. Table III, however, indicates concentrations of C, D, and E which are well above concentrations of solvent impurities expected to be present.

b. We are observing reaction of the solvent with oxides of nitrogen or photochemical intermediates.

c. There is a genuine solvent effect.

The photolysis of 1-hydroxypyrrolidine proceeded very slowly in isopentane solution. Thus if it were present, it should have been detected. Although peak J appeared very close to the hydroxylamine in the gas chromatogram, further examination revealed their retention times were not identical.

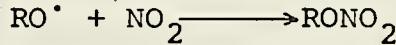
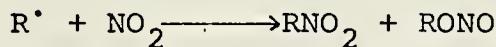
3. Photolysis in Cyclohexane

A solution of the nitramine (10^{-2}) was photolysed as described previously. Only one product was found to be present. The retention time did not correspond to any observed previously. Although there was no strong ultraviolet absorption maxima greater than 200 nm there did seem to be weaker $n \rightarrow \pi^*$ absorptions present at longer wavelengths. This suggests the presence of an atom with an unshared electron pair. The IR indicated that no alcoholic, olefinic, or aromatic protons were present. There was, however, an intense absorption at 1622 cm^{-1} . The only class of compounds apparently consistent with this data were alkyl nitrates. The IR

of peak Z agreed well with a previously published spectra of cyclohexylnitrate, which is given below [42]:

1626 (vs)	1280 (vs)	1093 (vw)	902 (m)
1464 (m)	1239 (vw)	1034 (w)	870 (vs)
1369 (vw)	1195 (vw)	1007 (m)	843 (m)
1355	1160 (vw)	942 (m)	803 (vw)
1322 (w)	1121 (vw)	921 (w)	957 (w)
			692 (w)

The bands observed in the IR of the collected product at 1547 and 1360 cm^{-1} are believed to belong to a nitro compound present as an impurity. The reaction of various nitrogen oxides with cyclohexane to give cyclohexyl nitrates has been observed previously [43-45]. Although the mechanism of this reaction remains obscure, the following schemes are suggested:



C. MOLECULAR ORBITAL CONSIDERATIONS

Much information about the photophysical processes occurring in nitramines may be obtained from examination of the simpler nitro chromophore, which has been well documented [46].

The nitro group may be represented by the equivalent resonance structures shown in Figure 12. The nitrogen atom has an sp^2 configuration, two of the three sigma bonds being

attached to equivalent oxygen atoms (Figure 13). Of the five nitrogen electrons, two are assigned to a P_{π} orbital and three are assigned to σ orbitals. Each oxygen atom has six valence electrons, two being assigned to a low energy s orbital, two to a non-bonding p orbital, one to a σ bond, and one to a P_{π} orbital. Thus, there are four electrons delocalized over a three atom pi system. These three atomic orbitals combine to form three molecular orbitals, bonding, non-bonding, and anti-bonding, as shown on the energy level diagram in Figure 14. Appearing at the bottom of the diagram are the two lone pair s orbitals of the oxygens, split due to the proximity to the two oxygen atoms. Appearing at a higher energy are the corresponding two p orbitals. Although initially degenerate with the non-bonding pi orbital, these also are split due to non-bonded interactions. The ultraviolet spectrum of nitromethane consists of two bands; a band at 210 nm ($\log \epsilon = 4.2$) which is assigned as a $\pi_2 \rightarrow \pi_3$ transition, and a weaker band at 270 nm ($\log \epsilon = 1.3$), which is assigned as $n_a \rightarrow \pi_3$. One would expect to find the remaining transitions in the far ultraviolet.

The N-nitrochromophore is completely analogous except that there are now six electrons delocalized over a four atom pi system (see Figure 15). These four atomic orbitals combine to form four molecular orbitals, two bonding, one non-bonding, and one anti-bonding. The energy level diagram is shown in Figure 16. The $\pi_3 \rightarrow \pi_4$ transition is known to occur

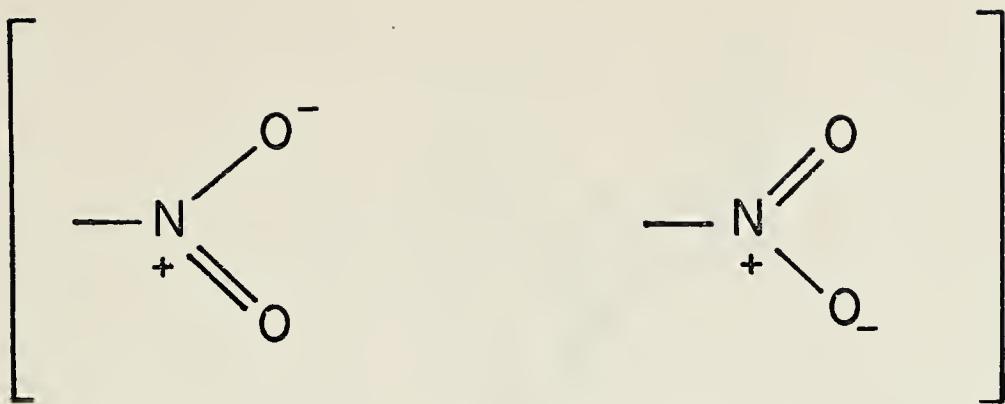


Figure 12. Resonance Structures for Nitro Group

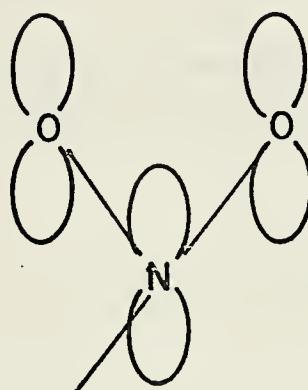


Figure 13. Orbital Representation of Nitro Group

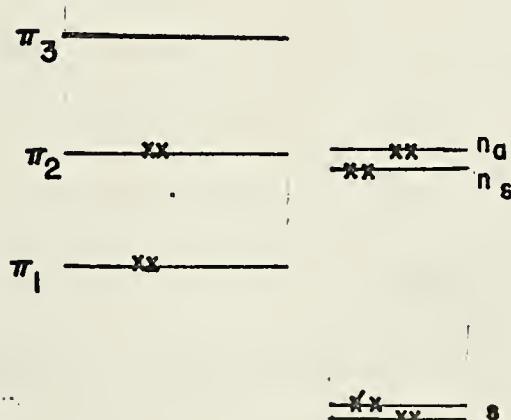


Figure 14. Energy Level Diagram for Nitro Group

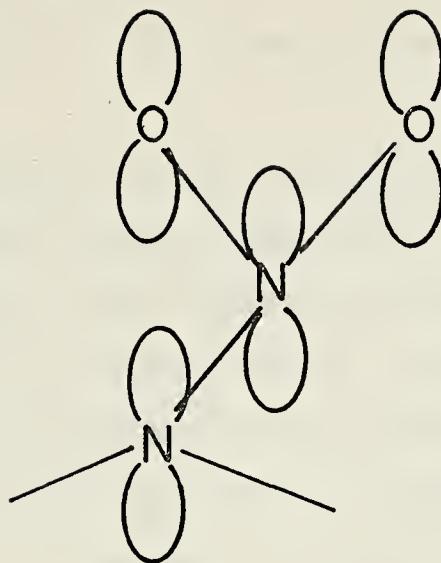


Figure 15. Orbital Representation of Nitramine Chromophore

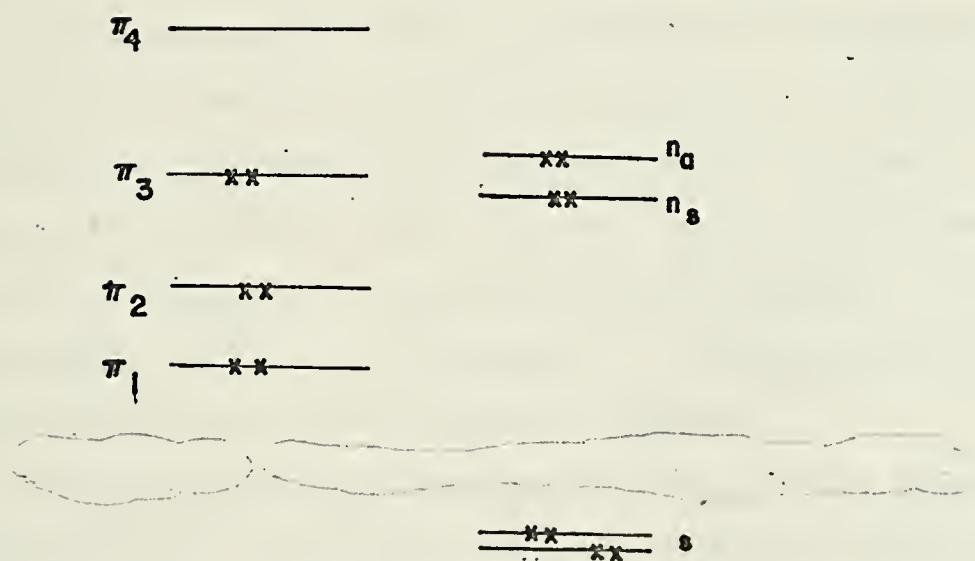


Figure 16. Energy Level Diagram for Nitramines

at 240 nm for 1-nitropyrrolidine. By analogy with nitromethane, we would expect to find the $n_a \longrightarrow \pi_4$ transition somewhere near 300 nm.

The discussion thus far has not considered the effect of electron spin. When electron-electron interactions are considered, singlet and triplet states are split, the triplet becoming the lower in energy. Due to a larger amount of spatial overlap, the singlet-triplet energy splitting is greater for π, π^* states than for n, π^* states [47]. Thus, in our case we cannot be sure about the identity of the lowest triplet state. The energy level diagram along with the photo-physical processes most probably occurring is illustrated in Figure 17. Since we have no knowledge about the nature of the excited state from which the reaction is occurring, we must accept the fact that it may be either a π, π^* or n, π^* state.

Simple molecular orbital calculations may give useful information about the nature of excited states. Various authors [43, 49] have described in detail the Hückel Molecular Orbital Method, which uses the " π -electron approximation" in which the π electron system is assumed to act independently of σ bonding framework. The approximation is valid generally only for planar π systems.

One must make additional corrections for the effect of hetero atoms. Streitwieser [49] has suggested making appropriate changes in the empirical coulomb integrals and resonance integrals associated with each atom and bond. His corrected values are shown below.

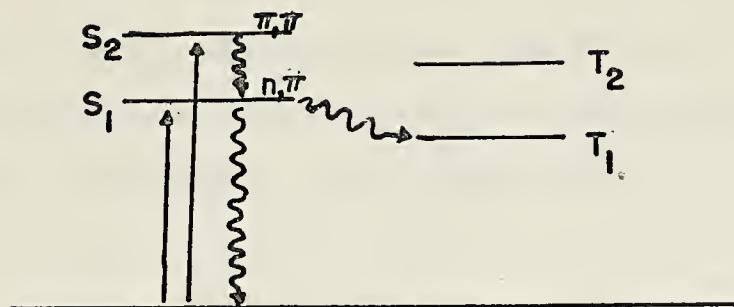


Figure 17. Primary Photophysical Processes in Nitramines

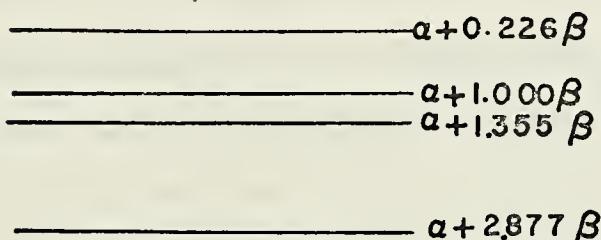


Figure 18. Molecular Orbital Energies for Nitramine Chromophore

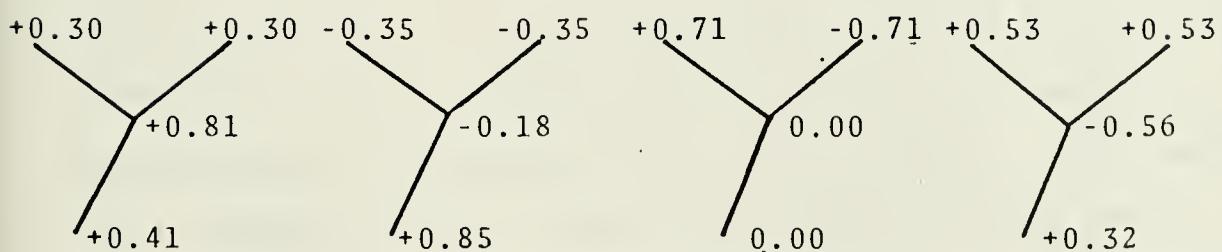


Figure 19. Nodal Diagram for Molecular Orbitals of the Nitramine Chromophore

$$\alpha_x = \alpha_o + h_x \beta_o$$

$$\beta_{cx} = k_{cx} \beta_o$$

where h_x and k_{cx} are empirical parameters which depend upon the identity of the hetero atom X, and the nature of the C-X bond. Using the values shown below,

$$h_0 = 1.0$$

$$h_{N1} = 1.5$$

$$h_{N2} = 2.0$$

$$k_{NO} = 0.8$$

$$k_{N=N} = 0.7$$

the system eigenvalues are obtained by diagonalization of the Hamiltonian matrix. The energy levels so obtained are given in Figure 18. The bond orders were calculated from the system eigenvectors, [49] and are shown below for the ground state and the first excited state.

$$P_{N-N} = 0.361 \quad P_{N-O} = 0.606$$

1st Excited state Total Resonance Energy = 9.730

$$P_{N-N} = 0.181 \quad P_{N-N} = 0.302$$

The above refer to $\pi \rightarrow \pi^*$ transitions. For the $n \rightarrow \pi^*$ transition, one might calculate bond orders in a similar fashion assuming seven electrons in the π system. The results are identical with the results of the first excited state given above. Thus, regardless of the identity of the lowest excited state, simple molecular orbital theory clearly predicts photochemical cleavage of the N-N bond.

The above treatment assumes the geometry of the excited state to be planar, and identical to that of the ground state. This assumption is frequently incorrect [46]. It is often found that the molecule in the excited state becomes non-planar to avoid unfavorable interaction between p orbitals. The nodal structures of the four π orbitals are given in Figure 19. As can be seen, rotation about the N-N bond would result in a large destabilization of the π_1 orbital, and moderate stabilization of the π_2 and π_4 orbitals. The extent of rotation about the N-N bond in the excited state will depend upon whether the energy lowering obtained from non-interaction of p orbitals compensates for the resonance energy which is lost. To answer the question, one must resort to more sophisticated molecular orbital treatment.

D. MECHANISTIC IMPLICATIONS

Photolysis of the nitramine never gave any of the products expected from the proposed mechanism. The hydroxylamine was never observed even though it was shown to be reasonably stable under the conditions of the photolysis but in the absence of NO_x . Furthermore, 1-pyrrolidone, expected to be the major photochemical endproduct, was never isolated or detected. It therefore appears that the mechanism, as proposed, is not likely.

The simple molecular orbital calculations indicate that photochemical cleavage of the N-N bond is expected rather than photochemical cleavage of the N-O bond. We do not expect the photoexcitation to have a significant effect on the C-N σ bond as the excitation is isolated on the nitramine chromophore and involves primarily the π electron system. In addition, the N-N single bond is roughly on the order of 30 Kcal/mole weaker than the C-N single bond [50]. Cleavage of the N-N bond is therefore expected to be the primary photophysical process occurring.

This is supported by the reaction of the nitrogen oxides formed with cyclohexane. Furthermore, Bodnar [10] observed the nitroxide radical in solution, giving evidence that the five membered ring remains intact; although the possibility of that being a side reaction is not resolved.

It was shown that the nitrogen oxides formed from the photolysis in cyclohexane react with solvent to give cyclohexyl nitrate as the only observed product. With hexane and

isopentane, more than one product would be expected due to differing positions of attack on the solvent molecule. This is in keeping with the differing products (C, D, E, and H, I, J, K, L) which were seen in each solvent.

It is difficult, however, to explain the transient peaks B and G on the basis of solvent reaction with nitrogen oxides. It seems unlikely that both solvents would react with the nitrogen oxides present to give products having identical retention times. Lower molecular weight alkyl nitrates have boiling points considerably lower than those of higher molecular weight. For example, cyclohexyl nitrate distills at 70°C/4 mm while neopentyl nitrate distills at 28°C/7 mm. Furthermore, the cyclohexyl nitrate was formed in "large" quantities in solution, and seemed fairly stable under the photochemical conditions. This is in direct contrast to the photochemical behavior B and G.

The identity of product B remains unknown. From its retention time on the gas chromatogram, it is apparent that it is of high molecular weight and relatively nonvolatile. That it was seen in two different solvents seems to indicate that it is not due to reaction with solvent. Two possibilities which remain are the reaction of pyrrolidine radicals (X) with oxides of nitrogen, and the coupling of pyrrolidine radicals to give XI.

From the studies in isopentane and hexane, it is apparent that molecule B decomposes photochemically to give products which are not seen, as the quantity of products (C, D, E and H, I, J, K, L) observed was much smaller than the quantity of starting material. The nitroxide radical observed by Bodnar [10] seems to indicate some reaction of the pyrrolidine radical with nitrogen oxides. Whether or not the nitroxide radical is involved as a major photochemical intermediate remains in question.

As for the decomposition of HMX, we expect the primary photochemical process to be cleavage of an N-N bond to give the corresponding N radical. Thus the mechanisms proposed by Maycock and Trobit for the photochemical decomposition seem unlikely.

LIST OF REFERENCES

1. Fordham, S., High Explosives and Propellants, p. 37, Permagon Press, 1966.
2. Urbanski, Tadeusz, Chemistry and Technology of Explosives, V. III, p. 77, Permagon Press, 1967.
3. Bachman, W. E., and Sheehan, J. G., "A New Method of Preparing the High Explosive RDX," Journal of the American Chemical Society, v. 71, p. 1842-1845, May 1949.
4. Robertson, A. J. B., "Thermal Decomposition of Explosives. II. Cyclotrimethylenetrinitramine (Cyclonite) and Cyclo-tetramethylenetrinitramine," Transactions of the Faraday Society, v. 45, p. 85-93, January 1949.
5. Maksinov, Yu. Ya., "Thermal Decomposition of Hexogen and Octogen," Transcripts of the Moscow Chemical and Technological Institute, v. 53, p. 73-84, 1967.
6. Suryanarayana, B., Graybush, R. J., and Autera, J. R., "Thermal Degradation of Secondary Nitramines: A Nitrogen-15 Tracer Study of HMX (1,3,4,7-Tetranitro-1,3,5,7-tetrazacyclooctane)," Chemistry and Industry, v. 52, p. 2177-2178, 30 December 1967.
7. Suryanarayana, B., Autera, J. R., and Graybush, R. J., "Effect of Ultraviolet Irradiation of Phase Transformations in Octahydro 1,3,5,7-Tetranitro-1,3,5,7-tetrazocine Polymorphs," Molecular Crystals, v. 2(4), p. 373-377, 1967.
8. Maycock, J. N., Pai Vernaker, V. R., and Lochte, W., "Physio-Chemical Properties of 1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane (HMX) II. Spectra and Ultraviolet Radiation Damage Phenomena," Physica Status Solidi, v. 35, p. 849-860, 1960.
9. Torbit, J. B., The Photochemical Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane, Masters Thesis, Naval Postgraduate School, Monterey, California, 1970.
10. Bodnar, J. W., The Photochemistry of Nitramines I: Preparation of Nitroxides in Solution in situ in Single Crystals, Masters Thesis, Naval Postgraduate School, Monterey, California, 1971.

11. Whittaker, H., Photochemistry of Nitramines II: Stoichiometry, Intermediates, and Products, Masters Thesis, Naval Postgraduate School, Monterey, California, 1971.
12. Moon, R. L., Photochemistry of Nitramines III: Some Potential Intermediates, Masters Thesis, Naval Postgraduate School, Monterey, California, 1972.
13. Bodnar, J. W., and Rowell, C. F., "ESR Studies of Unsubstituted Cyclic Nitroxides in Solids," Journal of Chemical Physics, v. 56, p. 707-709, 1971.
14. Dupeyre, R. M., and Rassat, A., "Nitroxides XIX. Norpusuedo-pelletierine-N-Oxyl, a New, Stable, Unhindered Free Radical," Journal of the American Chemical Society, v. 88, p. 3180-3181, 1966.
15. Adamic, K., Bowman, D. F., and Ingold, K. U., "Self-Reaction of Diethylnitroxide Radicals," Journal of the American Chemical Society, v. 92, p. 1093-1094, 1970.
16. Adamic, K., Bowman, D. F., Gillam, T., and Ingold, K. U., "Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. I. Self-Reactions of Diethylnitroxide Radicals," Journal of the American Chemical Society, v. 93, p. 902-908, 1971.
17. Keana, J. F. W., Dinerstein, R. J., and Baitis, F., "Photolytic Studies on 4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, a Stable Nitroxide Free Radical," Journal of Organic Chemistry, v. 36, p. 209-211, 1971.
18. Bowman, D. F., Gillan, T., and Ingold, K. U., "Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. III. Self-Reactions of Dialkylnitroxide Radicals," Journal of the American Chemical Society, v. 93, p. 6555-6561, 1971.
19. Weil, J. T., and Windle, J. J., "Electron Spin Resonance Study of Nitroxide Radicals from diethylhydroxylamine, Dioctylhydroxylamine, and N-Hydroxypyrrrolidine," Nature, v. 217, p. 842-843, 1968.
20. Windle, J. J., Kunhle, J. A., and Beck, C. H., "ESR Study of Interconversion in Substituted Piperidine Iminoxyls," Journal of Chemical Physics, v. 50, p. 2630-2656, 1969.
21. Bonnett, R., Clark, V. M., and Sir Alexander Todd, "Experiments Toward the Synthesis of Corrins. Part III. Formation of a Bicyclic Oxaziran from a Δ^1 -Pyrroline and from the Corresponding Nitrone," Journal of the Chemical Society, p. 2102-2104, 1959.

22. Kaminsky, L. S., and Lamchen, M., "Nitrone. Part III. Photolysis of Cyclis Nitrone," Journal of the Chemical Society (C), p. 2295-2299, 1966.
23. Emmons, W. D., "The Preparation and Properties of Oxazirines," Journal of the American Chemical Society, v. 79, p. 5739-5754, 1957.
24. Kaminsky, L. S., and Lamchen, M., "Nitrone. Part VI. The Pyrolysis of Oxaziridines Derived by Photolysis of Cyclic Nitrone," Journal of the Chemical Society (C), p. 2128-2130, 1967.
25. Fieser, L. F., and Fieser, M., Reagents for Organic Synthesis, John Wiley and Son, Inc., 1968.
26. Wiberg, K. B., Laboratory Technique in Organic Chemistry, p. 240, McGraw-Hill, 1960.
27. Coburn, M. D., and Ungnade, H. E., "Synthesis and the Structure of the N-Nitropyrrolidinones (1)," Journal of Heterocyclic Chemistry, v. 2, p. 308-309, 1965.
28. Adelman, R. L., "Studies on the Base Strength of N,N-Di-substituted Amides," Journal of Organic Chemistry, v. 29, p. 1837-1844, 1964.
29. Bottini, A. T., and Roberts, J. D., "Nuclear Magnetic Resonance Spectra. Nitrogen Inversion Rates of N-Substituted Aziridines (Ethylenimines)," Journal of the American Chemical Society, v. 80, p. 5203-5208, 1958.
30. Handbook of Chemistry and Physics, 45th ed., Chemical Rubber Company, 1964.
31. Duffield, A. M., "Mass Spectrometry in Structural and Stereochemical Problems. LXIII. Hydrogen Rearrangement Induced by Electron Impact on N-n-Butyl and N-n-Pentyl Pyrroles," Journal of American Chemical Society, v. 87, p. 805-810, 1965.
32. Yurev, Yu. K., and others, Zhur. Obschei Khim. (J. Gen. Chem.) 19, 1730-1733 (1949); cf. Uchenye Zapiski Moskov Gosudarst Univ. no. 79 (1945); C. A., v. 44, 1482e, 1950.
33. de Jong, Meta, and Wibout, J. P., "Ueber die Katalytische Hydrierung von Pyrrolen zu Pyrrolidinen," Recueil des Travaux Chemiques des Pays-Bas, v. 49, p. 237-246, 1930.
34. Thesing, J., and Sirrenberg, W., "Cyclische Nitrone, IV. Darstellung und Eigenschaften des Δ^1 -Pyrrolin-N-Oxyds," Chemische Berichte, v. 92, p. 1748-1755, 1959.

35. Cope, Arthur C., and Lee, Hiok Huang, "Amine Oxides. II. Conversion to N,N-Dialkylhydroxylamines," Journal of the American Chemical Society, v. 79, p. 964-965, 1957.

36. Cope, A. C., and Trumbull, E. R., "Olefins from Amines: The Hoffmann Elimination Reaction and Amine Oxide Pyrolysis," Organic Reactions, v. 11, p. 317-401.

37. Zinner, G., and Moll, R., "Zur Kenntnis der 1-Alkoxy-2,4-dioxoazetidine," Chemische Berichte, v. 89, p. 1292-1298, 1966.

38. Cope, A. C., Foster, T. T., and Towle, P. H., "Thermal Decomposition of Amine Oxides to Olefins and Dialkylhydroxylamines," Journal of the American Chemical Society, v. 71, p. 3929-3935, 1949.

39. Cope, A. C., and Lebel, N. C., "Amine Oxides. VII. The Thermal Decomposition of the N-Oxides of N-Methylazacycloalkanes," Journal of the American Chemical Society, v. 82, p. 4656-4662, 1960.

40. Rogers, M. A. Thorlod, "Aliphatic Hydroxylamines. Part I. Preparation," Journal of the Chemical Society, p. 769-772, 1955.

41. Wernick and Wolfenstein, Ber., 31, p. 1953, 1898.

42. Urbanski, T., and Witanowski, M., "Infra-Red Spectra of Nitric Esters," Faraday Society Transactions, v. 59, p. 1039-1045, 1963.

43. Titov, A. I., and Shchitov, N. V., "Mechanism of Nitration of Paraffins and Cycloparaffins with Nitric Anhydride," Doklady Akad Nauk S. S. R. 81, 1085-8, 1952; C. A., v. 46, 7992i, 1952.

44. Titov, A. I., and Matveeva, M. K., "Mechanism of Nitration and Oxidation of Cyclohexane," Doklady Akad. Nauk S. S. R. 83, 101-104 (1952); C. A., v. 47, 2715b, 1953.

45. Denisov, E. T., and Emanuel, N. M., "Gaseous Initiation by Nitrogen and Oxidation of Cyclohexane in the Liquid Phase," Zhur. Fiz. Khim., 31, 1266-1275, 1957; C. A., v. 52, 3485d, 1958.

46. Jaffe, H. H., and Orchin, Milton, Theory and Applications of Ultraviolet Spectroscopy, John Wiley and Sons, Inc., 1962.

47. Turro, N. J., Molecular Photochemistry, W. A. Benjamin, Inc., 1967.

48. Wiberg, K. B., Physical Organic Chemistry, John Wiley and Sons, Inc., 1966.
49. Streitweiser, A., Molecular Orbital Theory for Organic Chemists, John Wiley and Sons, Inc., 1967.
50. Roberts, J. D., and Caserio, M. C., Basic Principles of Organic Chemistry, W. A. Benjamin, Inc., 1965.

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ABSTRACT

1-Nitropyrrolidine upon irradiation with ultraviolet light is known to undergo photochemical decomposition. This investigation is concerned with the mechanism and products of the reaction.

A potential intermediate was synthesized and found not detectable in the photochemical system. A product of the photolysis in alkane solutions was identified as an alkyl nitrate. Gas chromatographic analysis and a molecular orbital calculation provided information to suggest processes which might be occurring.

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1-Hydroxypyrrrolidine						
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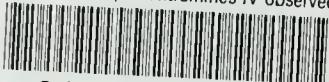
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